S.L/.26-4-g-3

The Royal College of Physicians
of London.

From the Library of
Sir Andrew Clark, Bart.
Presented by Lady Clark.
147 D 24

With the Author's Compliments

HANDBOOK

OF

MODERN CHEMISTRY

INORGANIC AND ORGANIC.

For the use of Students.

BY

CHARLES MEYMOTT TIDY, M.B., F.C.S.,

Professor of Chemistry & of Medical Jurisprudence & Public Health at the London Hospital;
One of the Official Analysts to the Home Office;
Medical Officer of Health for Islington;
Late Deputy Medical Officer of Health and Public Analyst for the City of London;
Master of Surgery, &c., &c., &c.

(*SECOND EDITION, REVISED AND ENLARGED.*)

COLLEGE OF PHYSICIANS

LONDON:
SMITH, ELDER & CO., 15 WATERLOO PLACE.
1887.

(*All rights reserved.*)

LONDON:
WERTHEIMER, LEA AND CO., PRINTERS,
CIRCUS PLACE, LONDON WALL.

ROYAL COLLEGE OF PHYSICIANS LIBRARY

CLASS	54
ACCN.	25208
SOURCE	
DATE	

TO

THOMAS HAWKSLEY, Esq., C.E., F.R.S., etc.,

Past President of the Institutions of Civil and Mechanical Engineers.

Dear Mr. Hawksley,

After several years of work, interrupted by the demands of an active professional life, I venture to submit to the public a new edition of my Handbook of Chemistry. If excuse be needed for another issue of a work that has been out of print for some years, I may claim the rapid sale of the first edition, which appeared in 1878.

As regards general arrangement, I have adhered to the plan I first adopted. That it has advantages is indicated, I may reasonably infer, by the fact that it has had its imitators. I have, however, made certain important alterations. I have omitted, not without some regret, the constitutional formulæ first suggested by Dr. Frankland, which for three years I adopted in my lectures. On the whole, it seems preferable, in view of the many-sided relationships of different chemical compounds, to avoid their systematic expression by any single scheme of constitutional formulæ, necessarily representing them in a single aspect only.

With respect to the names of chemical compounds, I have at times not hesitated to write in common language. If I have used the word "potash," and the body I mean to imply thereby is understood, I am satisfied. I confess that the growing necessity for having a translation at one's side in attempting to understand the modern scientific paper, is in my opinion a circumstance to be deplored. Danger, moreover, is always to be apprehended when a language has to be invented to support a theory or a formula. A party shibboleth has, no doubt, a charm for its special clique. It serves as a bond of union for the initiated, whilst it prevents the interference of outsiders. But, all the same, it is distracting to the independent worker, and can but prove a hindrance to the general cultivation of science.

I dedicate this book to you without asking your permission. Few subjects are discussed in its pages which do not bear marks of your accurate criticism. I ask you to accept the dedication as an acknowledgment on my part of the kindly assistance you, more than any one, have accorded me in my professional career. And if, as is the case, professional association has begotten affectionate regard, then I venture to think no other explanation is required for offering you the best expression I can of sincere esteem and gratitude.

Believe me,
My dear Mr. Hawksley,
Sincerely yours,
C. MEYMOTT TIDY.

3, Mandeville Place,
Cavendish Square,
August, 1887.

P.S.—I desire to acknowledge my indebtedness to my friend and assistant, Mr. J. H. Bicket, F.C.S. The labour of correcting the proof sheets would have been exceedingly greater but for his ready and intelligent assistance.

PREFACE TO THE FIRST EDITION.

When an author writes a new book on a subject upon which so many good books have been already written, he is expected to give some reason for doing so.

I venture, therefore, to plead my apology for the publication of these outlines of Chemistry. Within three months of graduating—in other words, when "fresh from the schools"—I was appointed Joint Lecturer on Chemistry with the late Dr. Letheby at the London Hospital. Consequently, my first lecture-notes were prepared when familiar by practical experience with the wants of a student. Year by year, these notes have been added to, and, to some extent, re-written; nevertheless, except in a few instances, I have strictly adhered to the plan I first adopted. I submit these lecture-notes to the profession as the joint experience of a student and a teacher.

In the *first* section of this work, I have considered the chemistry of the non-metals; in the *second*, the chemistry of the metals; and, in the *third*, the chemistry of organic bodies.

Before proceeding to details, I have in each case generalized largely on the subject matter of the section. Thus, as introductory to the science of chemistry generally, and before describing the non-metals, I have discussed at some length the subject of chemical affinity. In a similar manner, I have generalized on the metals and on the chemistry of organic bodies, before proceeding to the consideration of the several elements or compounds comprehended under the section. Nothing to my mind is more important than for teachers and students to grasp the notion that the lecture-room is not the same as the study—in other words, that the lecture will not take the place of the book, any more than the book can take the place of the lecture. Each has its special work in education. Thus it appears to me that in the lecture-room the work of the teacher is best fulfilled by sketching accurately, yet broadly, the general outlines of the whole subject, intensifying them where necessary by illustration and experiment (in fact, so to speak, covering the canvas), leaving the student, in the quiet book-work of the study, to fill in the minute details for himself. With this view of the different functions of lectures and books, I have always adopted in the lecture theatre a system of broad generalization, such as I have briefly shadowed forth in the remarks preceding the several sections. I hope these may prove of general use as an introduction to the detailed work that follows, but they are mainly intended as a guide to my own pupils at lecture.

Thus much for introductory generalisation.

As regards the details, my aim has been to be methodical. I have therefore considered each element, and, as far as possible, each compound, under the several heads of (1.) History, (2.) Natural History, (3.) Preparation, (4.) Properties, (*a*.) Sensible, (*β*.) Physical, and (*γ*.) Chemical; (5.) Uses in Medicine and in the Arts and Manufactures, and (6.) Tests.

In dealing with the non-metals I have commenced with oxygen and finished with hydrogen, discussing under each element the compounds it forms with the elements previously considered in detail. Thus, for example, under hydrogen (the last of the non-metals discussed), I have described all the compounds that it forms with the non-metals.

* * * * * * * *

As regards notation, although I recognise great advantages in that suggested by Dr. Frankland, I am by no means prepared to abandon the old formulæ. Under these circumstances I have, in the inorganic portion of the work, stated equations in both molecular and constitutional formulæ.*

In the case of each metal I have drawn up a table of its most important compounds, their formulæ, and such tabulated information respecting them as I thought might prove useful to the student.

My first object in this book is that it should serve as a manual for students. As a medical man and a professor in a medical school, I have always made a special point of noting in my lectures the bearing of chemical science on medicine. This will account to the general student of chemistry for my discussing certain subjects in greater detail than is usual in similar works.

Further, bearing in mind the special knowledge required of medical officers of health in dealing with nuisances arising from various trade operations, I have given the outlines (limited of course to the strictly scientific details) of most manufacturing processes, and the chemical reactions involved in the same. To cure a nuisance is more scientific than to annihilate a manufactory, and to suggest the cure we must accurately understand the case.

---

* In this edition, as stated in the Dedication, the constitutional formulæ have been omitted.

To the lecture-notes of Frankland and to the manuals of Chemistry of Odling, Williamson, Roscoe, Bloxam, Thorpe, Miller, and Fownes, and particularly to the excellent manual on Organic Chemistry, by Dr. Armstrong, I desire to express my obligations.

I should wish to add that, although I have spared no pains to render this Handbook as complete and as accurate as possible, nevertheless I trust some allowance will be made for unavoidable errors arising from the circumstance that it has been written amidst the constant interruptions of professional work. Not unfrequently indeed has it had for a time to be laid aside altogether, thereby rendering continuity of thought and uniformity of treatment a matter of some difficulty.

April, 1878.

CONTENTS.

CHAPTER I.

PAGE

CHEMICAL AFFINITY : Definition—Conditions necessary for its exertion—Phenomena — The Circumstances influencing its Action — Influence of Gravitation, Cohesion, Elasticity and Adhesion—Solution—Surface Action—Nascent Condition of Matter—Influence of Quantity and of Mechanical Force — Catalysis — Concurrent Attractions — Influence of Heat and Cold—Dissociation— Thermo-Chemistry—Influence of Light and of the Electric Current—Electrolysis—Influence of Vital Action—Methods of estimating the energy of the force 1

CHAPTER II.

Nomenclature—Elements and Compounds— Names of Bodies— Chemical Symbols and Formulæ — Combining Proportions —Atomic Theory—Atoms — Molecules —Atomic and Molecular Combination—Compound Radicals — Volume — Standard Pressure and Temperature — Relative Weight — The Crith, a unit of Volume — Relation between Atomic Weight and Specific Gravity—Relation between Atomic Weight and Specific Heat — Atomicity and Quantivalence — The Periodic Law—Chemical Formulæ—Substitution — Isomerism — Isomorphism — Allotropism—The Metric System 27

CHAPTER III.

Crystallization 65

SECTION I.—THE NON-METALS.

CHAPTER IV.

OXYGEN.

OXYGEN : Synonyms—History—Natural History—Preparation—Properties. OZONE : History—Natural History—Preparation—Properties—Tests—Quantitative Determination—Antozone—Uses of Oxygen—Respiration—Combustion 68

CHAPTER V.

FLUORINE—CHLORINE—BROMINE—IODINE.

The Halogens or Haloid Elements : FLUORINE. CHLORINE : Compounds of Chlorine and Oxygen—Hypochlorous anhydride—Hypochlorous acid—Chlorous acid — Chloric peroxide — Chloric acid — Perchloric acid. BROMINE : Compounds of Bromine with Oxygen and Chlorine. IODINE : Compounds of Iodine and Oxygen—Iodic anhydride—Iodic acid—Periodic acid—Compounds of Iodine and Chlorine—Generalization on the Halogens 86

PAGE

CHAPTER VI.

NITROGEN.

NITROGEN: Atmospheric Air—Its Constituents—Compounds of Nitrogen and Oxygen—Nitrous oxide—Hyponitrous acid—Nitric oxide—Nitrous anhydride—Nitrous acid—Nitric peroxide—Nitric anhydride—Nitric acid—Compounds of Nitrogen and the Haloids—Compounds of Nitrogen with Oxygen and the Haloids—Chloride of Nitrogen—Iodide of Nitrogen—Nitrous oxychloride—Nitrylic chloride—Chloro-nitric gas . 115

CHAPTER VII.

PHOSPHORUS.

PHOSPHORUS: Compounds of Phosphorus and Oxygen—Suboxide of Phosphorus—Hypophosphorous acid—Phosphorous anhydride—Phosphorous acid — Phosphoric anhydride—Metaphosphoric acid — Pyrophosphoric acid—Orthophosphoric acid—Compounds of Phosphorus and the Haloids —Phosphorous Chloride—Phosphoric Chloride—Phosphoric Oxychloride—The Iodides of Phosphorus—Phospham—Action of Ammonia on Phosphorus Compounds. 149

CHAPTER VIII.

SULPHUR—SELENIUM—TELLURIUM.

SULPHUR: Compounds of Sulphur with Oxygen (Sulphur Acids) — Sulphurous anhydride and acid—Sulphuric anhydride and acid—Persulphuric anhydride—Thiosulphuric acid—Dithionous acid—Dithionic acid—Trithionic acid — Tetrathionic acid — Pentathionic acid — Compounds of Sulphur and Chlorine—Compounds of Sulphur, Oxygen, and the Haloids—Compounds of Sulphur and Phosphorus. SELENIUM: Compounds of Selenium and Oxygen. TELLURIUM: Compounds of Tellurium and Oxygen 171

CHAPTER IX.

CARBON—BORON—SILICON.

CARBON: Coal—Compounds of Carbon and Oxygen—Compounds of Carbon and the Haloids—Compounds of Carbon with Oxygen and the Haloids —Compounds of Carbon with Sulphur and with Sulphur and Oxygen. BORON: Boric Acid—Compounds of Boron with Nitrogen, the Haloids, and Sulphur. SILICON: Compounds of Silicon with Oxygen, with the Haloids, with Nitrogen, and with Sulphur 198

CHAPTER X.

HYDROGEN.

HYDROGEN: Compounds of Hydrogen and Oxygen—Water—Compounds of Hydrogen with the Haloids, with Nitrogen, with Phosphorus, with Sulphur and Selenium—Compounds with Carbon, viz., Methane, Ethylene and Acetylene—Coal gas—Flame—Compound of Hydrogen and Silicon—Compound of Hydrogen and Boron 227

PAGE

SECTION II.—THE METALS.

CHAPTER XI.

GENERAL REMARKS ON THE METALS.

Derivation and Definition of a Metal—Order of Discovery—Natural History—Physical and Sensible Properties—Chemical Properties—Classification 280

CHAPTER XII.

ALLOYS AND SALTS.

Alloys—Changes in property effected by Alloying—Acids—Bases—Salts—Oxides. *Haloid Salts*—Chlorides, Bromides, Iodides, Fluorides, Sulphides, Nitrides, Arsenides, Selenides, Tellurides, Phosphides, Carbides, Borides, Silicides, Hydrides. *Oxy-salts*—Sulphates, Selenates, Tellurates, Chromates, Manganates, Tungstates, Molybdates, Stannates, Tellurates, Thiosulphates, Sulphites, Selenites, Dithionates, Nitrates, Nitrites, Hyponitrites, Chlorates, Bromates, Iodates, Perchlorates, Periodates, Chlorites, Hypochlorites, Phosphates, Hypophosphites, Phosphites, Arsenates, Vanadates, Antimonates, Sulph-arsenates, Sulph-antimonates, Arsenites, Sulph-arsenites, Sulph-antimonates, Carbonates, Silicates, Borates. *Double Salts* 289

CHAPTER XIII.

THE ALKALINE METALS AND THEIR COMPOUNDS.

POTASSIUM : Gunpowder — SODIUM — LITHIUM — CÆSIUM—RUBIDIUM—AMMONIUM 339

CHAPTER XIV.

THE METALS OF THE ALKALINE EARTHS AND THEIR COMPOUNDS.

BARIUM—STRONTIUM—CALCIUM—MAGNESIUM 374

CHAPTER XV.

THE METALS—*continued.*

MANGANESE—IRON—CHROMIUM—ZINC—COBALT—Cobaltamines—NICKEL—URANIUM—INDIUM 391

CHAPTER XVI.

THE METALS OF THE EARTHS AND THEIR COMPOUNDS.

ALUMINIUM : The Alums — Clay—Porcelain and Pottery — GALLIUM — BERYLLIUM — THORIUM — ZIRCONIUM — CERIUM — DIDYMIUM — YTTRIUM — ERBIUM — TERBIUM — YTTERBIUM — SCANDIUM — SAMARIUM—DECIPIUM—NORWEGIUM—LANTHANUM 437

CHAPTER XVII.

THE METALS—*continued.*

A.—*Metals whose Sulphides are Insoluble in the Alkaline Sulphides.* COPPER—BISMUTH—CADMIUM—PALLADIUM—RHODIUM—OSMIUM—RUTHENIUM.

PAGE

B.—*Metals whose Sulphides are Soluble in the Alkaline Sulphides.*

TIN—TITANIUM—ANTIMONY—ARSENIC—VANADIUM—NIOBIUM—TANTALUM—GOLD—PLATINUM—Platinamines—MOLYBDENUM—IRIDIUM . 453

CHAPTER XVIII.

THE METALS—*concluded.*

LEAD—SILVER—MERCURY : Amalgams—THALLIUM—TUNGSTEN . . . 520

SECTION III.—ORGANIC CHEMISTRY.

CHAPTER XIX.

Organic Compounds and Organised Bodies—Definition of Organic Chemistry—ORGANIC ANALYSIS—Ultimate Analysis—Vapor Density—Method of determining Vapor Densities—Proximate Analysis 556

CHAPTER XX.

THE NATURAL AND ARTIFICIAL CHANGES OF ORGANIC BODIES.

A.—*Natural :* FERMENTATION—Varieties—I. Alcoholic—II. Lactic—III. Butyric—IV. Mucous—V. Acetous—Conditions necessary for Fermentation—Circumstances influencing Fermentation—Theories to account for it—Practical Applications. PUTREFACTION—Disinfectants—EREMACAUSIS.

B.—*Artificial :* Action of Heat on Organic Bodies—Distillation of Coal—Coal Gas—Products of the Distillation of Wood—Action of Acids—Action of Alkalies—Action of Haloid Elements—Action of Nascent Oxygen and Hydrogen and of other Reagents—Action of Light and Electricity 578

CHAPTER XXI.

CYANOGEN AND ITS COMPOUNDS.

CYANOGEN : Hydrocyanic Acid—Cyanides—Compounds of Cyanogen with the Haloids and with Hydroxyl—Sulphocyanic Acid—Double Salts of Cyanogen—The Nitroprussides—Prussian Blue—Reactions of Cyanogen Compounds 604

CHAPTER XXII.

THE HYDROCARBONS.

Series of Hydrocarbons : The Paraffins—Chloroform—The Olefines—The Acetylene Series—Turpenes—Benzenes—Naphthalene—Anthracene—Alizarin.

Supplementary Chapter : Paraffin and Petroleum—Turpentine—Volatile Oils—Camphors—Resins—Gum Resins—Oleo-Resins—Balsams—India Rubber—Gutta Percha 621

CHAPTER XXIII.

THE ALCOHOLS.

Relation of the Alcohols to other Bodies—Kolbe's classification—Series of Alcohols—General preparation and properties of the members of the various Series—Monohydric, Dihydric, and Trihydric Alcohols—Ethylic Series—The Phenols—The Glycols—Orcins—Mercaptans.

Supplementary Chapter : The Sugars—Glucosides—Starches—Gums—Reactions of various Alcohols and allied Bodies 658

PAGE

CHAPTER XXIV.

THE ORGANIC ACIDS.

Relationship to other bodies—Constitution. *Monobasic Acids:* Acetic Series—Acrylic—Sorbic—Benzoic—Cinnamic—Naphtoic. *Dibasic Acids:* Succinic—Fumaric—Phthalic. *Tribasic Acids:* Tricarballylic—Mesitic. Reactions of the acids.

Supplementary Chapter: Fats and Oils—Soaps—Candles—The Tannins—Ink—Tanning 692

CHAPTER XXV.

THE ETHERS.

Oxy-Ethers—Ethers of Monohydric Alcohols—Preparation—Ethers of Di- and Trihydric Alcohols. *Sulpho-Ethers. Haloid Ethers. Compound Ethers* 738

CHAPTER XXVI.

THE ALDEHYDES (Alcohol Dehydrogenatum).

Constitution—Preparation—Reactions—Aldehydes of the Acetic Series—Aldehydes of the Acrylic and Benzoic Series—Other Aldehydes . . 743

CHAPTER XXVII.

THE KETONES.

Constitution—General Preparation—Properties and Reactions . . . 748

CHAPTER XXVIII.

THE ALKALOIDS—AMMONIA DERIVATIVES.

The Amines—Amides—Imides—Alkalamides—Nitriles—Phosphines—Arsines—Stibines—Bismuthines—Kakodyl—Organo-Boron and Organo-Silicon Compounds—Organo-Metallic Compounds—The Natural Alkaloids, Vegetable and Animal—Constitution of the Alkaloids . . . 750

CHAPTER XXIX.

COLORING MATTERS.

Natural History—General Preparation and Properties—Yellows—Reds—Blues—Browns—Blacks.

Supplementary Chapter: Dyeing and Calico Printing . . . 783

CHAPTER XXX.

VEGETABLE CHEMISTRY.

Tissues of Vegetable—Cellulin—Vegetable Parchment—Gun Cotton—Woody and Corky Tissue—The Life of a Plant 789

CHAPTER XXXI.

ANIMAL CHEMISTRY.

Albuminoids.—I. Animal Solids—II. Nutrient Fluids—III. Digestion, and the Fluids concerned in it—IV. Excrementitious Products . . . 794

TABLES.

TABLE OF THE ELEMENTS.

NOTE.—1. The page after the Element refers to the page at which it is described.
2. The Non-metals are printed in Black type, and the Metals in Roman type.

Element.	Atomic Symbol with number, showing atoms in molecule.	Atomic Weight.	Atomicity.	Specific Heat.	Specific Gravity of Gas or Vapor. Air=1.	Specific Gravity of Solids and Liquids. Water=1.	Melting Point. ° F.	Boiling Point. ° F.	100 cubic inches of Gas or Vapor weigh in grains at 60° F. & 30 B.P.	Discoverer and Date of Discovery.
Aluminium (p. 437)	Al_2	27·5	IV.	0·2143	..	2·6	812·0	..	..	Wöhler, 1828.
Antimony (Stibium) (p. 487)	Sb_2	122·0	III., V.	0·0508	..	6·7	842·0	2642·0	..	Basil Valentine.
Arsenicum (p. 495)	As_4	75·0	III., V.	0·0814	10·6	5·90	Volatilizes before fusing at 356	..	329·12	Brandt, 1733.
Barium (p. 374)	Ba_2	137·0	II.	0·047	..	4·0	Below red heat	..	..	Davy, 1808.
Beryllium (Glucinum) (p. 447)	Be_2	9·4	II.	0·408	..	2·1	..	..	..	Wöhler, 1828.
Bismuth (464)	Bi_2	208·2	III., V.	0·0308	..	9·83	507·2	..	..	
Boron (p. 218)	B_2	11·0	III.	0·5 (?)	..	2·68	..	..	..	Davy, 1807.
Bromine (p. 102)	Br_2	80·0	I.	0·056	5·54	3·187	—12	145·4	..	Balard, 1826.
Cadmium (p. 468)	Cd	12·0	II.	0·057	3·94	8·604	442	1580	..	Stromeyer, 1818.
Cæsium (p. 366)	Cs_2	133·0	I.	..	..	1·88	77·8	..	..	Bunsen and Kirchhoff, 1860
Calcium (p. 379)	Ca_2	40·0	II.	0·167	..	1·578	Red heat	..	..	Davy, 1808.
Carbon (p. 198)	C_2	12·0	(II.) IV.	0·40	(?)	3·5	..	..	..	Pre-historic.
Cerium (p. 449)	Ce_2	140·5	II., IV.	0·045	..	6·7	..	..	..	Klaproth, 1803.
Chlorine (p. 88)	Cl_2	35·5	I.	0·18	27·4	..	..	..	76·076	Scheele, 1774.
Chromium (p. 411)	Cr_2	52·1	(II., IV.) VI.	0·12	..	7·31	..	..	..	Vauquelin, 1797.
Cobalt (p. 424)	Co_2	58·6	II. (IV.) VI.	0·11	..	8·50	..	..	..	Brandt, 1733.
Copper (Cuprum) (p. 453)	Cu_2	63·5	II.	0·0935	..	8·96	2426·0	..	..	Pre-historic.
Decipium (p. 451)	Dp_2	159·0	III.	..	..	..	..	..	..	Delafontaine.
Didymium (p. 450)	Di_2	146·0	III., V.	..	..	6·54	..	..	..	Mosander, 1841.
Erbium (p. 451)	Er_2	165·9	III.	..	..	..	..	..	..	Mosander, 1843.
Fluorine (p. 86)	F_2	19·0	I.	0·27	1·316	..	..	..	40·717	Davy, 1808.
Gallium (p. 446)	Ga_2	69·5	pseudo triad	0·080	..	5·935	86·27	..	..	Boisbaudran, 1875.
Gold (Aurum) (p. 505)	Au_2	196·7	I., III.	0·0324	..	19·4	2192·0	..	..	Pre-historic.
Hydrogen (p. 227)	H_2	1·0	I.	2·3	0·0693	..	..	..	2·134	Cavendish, 1766.
Indium (p. 434)	In_2	113·4	III.	0·057	..	7·4	349·0	..	..	Reich and Richter, 1863.
Iodine (p. 105)	I_2	127·0	I.	0·054	8·716	4·947	225·0	347·0	275·16	Courtois, 1812.
Iridium (p. 517)	Ir_2	198·0	II., IV.	0·033	..	22·38	..	..	..	Smithson Tennant, 1804.
Iron (Ferrum) (p. 398)	Fe_2	56·0	II. to VI.	0·11	..	7·8	..	..	..	Pre-historic.
Lanthanum (p. 452)	La_2	138·5	III.	0·045	..	6·136	..	..	..	Mosander, 1841.

Manganese (p. 391)	Mn_2	[illegible]	II. to VI.	0·12	..	8·0	White heat.	..	..	Gahn, 1780.
Mercury (Hydrargyrum) (p. 538)	Hg	200·0	II.	0·0319	6·97	13·56	37·9	675·0	216·09	Pre-historic.
Molybdenum (p. 514)	Mo_2	96·0	II., IV., VI.	0·0722	..	8·6	..	..	..	
Nickel (p. 428)	Ni_2	58·6	II., IV., VI.	0·11	..	8·9	..	..	..	Cronstedt, 1751.
Niobium (p. 504)	Nb_2	94·0	III., V.	..	..	4·06	..	..	..	
Nitrogen (p. 114)	N_2	14·0	I., III., V.	0·36	0·9713	..	..	..	30·002	Chaptal, 1789.
Norwegium (p. 452)	Ng_2	214	..	..	..	..	..	..	..	
Osmium (p. 474)	Os_2	198·6	II. to VIII.	0·031	..	21·4	..	..	..	Tennant, 1803.
Oxygen (p. 68)	O_2	16·0	II.	0·25	1·1086	..	..	..	34·288	Priestley, 1774.
Palladium (p. 470)	Pd_2	106·5	II., IV.	0·059	..	11·6	2480·0	..	..	Wollaston, 1803.
Phosphorus (p. 149)	P_4	31·0	III., V.	0·17	4·298	1·848	112 0	554	132·86	Brandt, 1669.
Platinum (p. 509)	Pt_2	197·4	II., IV.	0·0311	..	21·5	3632·0	..	..	Wood, 1741.
Potassium (Kalium) (p. 339) ..	K_2	39·0	I.	0·16956	..	0·865	144·5	Low red heat.	..	Davy, 1807.
Rhodium (p. 473)	Rh_2	104·0	II. to VI.	0·058	..	12·1	..	..	..	Wollaston, 1803.
Rubidium (p. 366)	Rb_2	85·3	I.	0·077	..	1·52	101·3	..	..	Bunsen and Kirchoff, [1860.
Ruthenium (p. 476)	Ru_2	104·4	II. to VIII.	0·061	..	11·4	..	..	..	Claus, 1846.
Samarium (p. 451)	Sm_2	150	III.	..	..	..	..	..	..	Boisbaudran.
Scandium (p. 451)	Sc_2	44	III.	..	..	..	..	..	..	Nilson, 1879.
Selenium (p. 194)	Se_2	79·0	II., IV., VI.	0·075	5·68	4·788	212·0	1292·0	176·08	Berzelius, 1817.
Silicon (p. 221)	Si_2	28·2	IV.	0·20	..	2·0	..	..	..	Davy, 1807.
Silver (Argentum) (p. 530) ..	Ag_2	108·0	I.	0·056	..	10·57	1904·0	..	..	Pre-historic.
Sodium (Natrum) (p. 352) ..	Na_2	23·0	I.	0·2934	..	0·972	207·7	1652·0	..	Davy, 1807.
Strontium (p. 378)	Sr_2	87·6	II.	0·074	..	2·54	..	..	..	Davy, 1808.
Sulphur (p. 171)	S_2	32·0	II., IV., VI.	0·16	2·23 at 1040° C.	2·05	239·0	836·0	68·76	Pre-historic.
Tantalum (p. 504)	Ta_2	182·0	III., V.	..	..	..	..	..	..	
Tellurium (p. 196)	Te_2	128·0	II., IV., VI.	0·047	9·0	6·2	900	..	279·0	Müller, 1782.
Terbium (p. 451)	Tr_2	148·8	..	..	..	..	..	..	..	
Thallium (p. 550)	Tl_2	204·0	I., III.	0·0325	..	11·91	561·0	Below white heat.	..	Crookes, 1861.
Thorium (Thorinum) (p. 449)	Th_2	231·4	II., IV.	0·038	..	7·8	..	..	..	Berzelius, 1829.
Tin (Stannum) (p. 478)	Sn_2	118·0	II., IV.	0·0562	..	7·28	442·4	2912·0	..	Pre-historic.
Titanium (p. 484)	Ti_2	48·0	II., IV.	0·13	..	5·3	..	..	..	Gregor, 1791.
Tungsten (Wolfram) (p. 553)	W_2	184·0	IV., VI.	0·033	..	19·13	..	..	..	Scheele, 1781.
Uranium (p. 431)	U_2	238·5	II., IV., VI.	0·038	..	18·4	..	..	..	Klaproth, 1789.
Vanadium (p. 503)	V_2	51·3	III., V.	..	..	5·5	..	..	..	Del Rio, 1801.
Ytterbium (p. 451)	Yb_2	172·8	..	..	..	..	..	..	..	Marignac.
Yttrium (p. 451)	Y_2	89·8	III.	0·095	..	..	..	..	..	Gadolin, 1794.
Zinc (p. 418)	Zn	65·3	II.	0·094	..	6·8—7·2	773·0	1,904	..	In 13th Century.
Zirconium (p. 449)	Zr_2	90·0	IV.	0·066	..	4·15	Infusible.	..	..	

A
HANDBOOK OF MODERN CHEMISTRY.

CHAPTER I.

CHEMICAL AFFINITY.

Definition—Conditions necessary for the exercise of Chemical Affinity—Phenomena—The Circumstances influencing its Action—Influence of Gravitation, Cohesion, Elasticity, and Adhesion — Solution — Surface Action — Nascent Condition of Matter—Influence of Quantity and of Mechanical Force—Catalysis—Concurrent Attractions—Influence of Heat and Cold—Dissociation—Thermo-Chemistry—Influence of Light and of the Electric Current—Electrolysis—Influence of Vital Action—Methods of estimating the Energy of the Force.

CHEMICAL affinity may be defined as a "force of attraction acting between two or more *dissimilar* particles brought within an inappreciable distance, whereby a *new* compound (*i.e*, a compound possessing properties dissimilar from those of its constituents) is formed." Thus, if *Iodine* (a black, poisonous substance) be chemically combined with *Potassium* (a silvery white metal), a compound (Potassium Iodide) results, which exhibits neither sensible, chemical, physical, nor physiological resemblance to the constituent elements. This change of property is the special characteristic of "Chemism" or "Chemical Affinity." *Gravitation* is the attraction between similar or dissimilar particles, and is capable of acting at an appreciable distance ; *cohesion* is the attraction between similar particles at an inappreciable distance ; *adhesion*, the attraction between dissimilar particles at an inappreciable distance ; but no change of property results to the matter on which these several physical forces of attraction are exerted.

The chemical force has received different names : Bergman termed it "*Elective Gravitation* ;" Azais, "*Molecular Gravitation* ;" Newton, "*Chemical Attraction or Action* ;" others, "*Chemism*" and "*Heterogeneous Affinity* ;" whilst Stahl invented the phrase "*Chemical Affinity*" (or simply "*Affinity*"), because he supposed that bodies which combined chemically must have something in common. As a fact, we know that, chemically, "like does not consort with like," but, *par excellence*, with unlike ; bodies the most opposite, as, for example, acids and alkalies, being the most disposed to combine.

I.—The Conditions necessary for the Exercise of Affinity.

(*a.*) *There must be two or more dissimilar particles.*—Chemical union cannot take place between iron and iron, nor between sulphur and sulphur. Iron and sulphur, on the contrary, are capable of chemical combination. Usually, the more chemically like the substances, the less intense is the play of affinity, and vice versâ. Thus, the constituents of most chemical compounds, when subjected to a battery current, pass to opposite poles—those attracted to the *positive* pole of the battery being termed *electro-negatives*, and those attracted to the *negative* pole, *electro-positives.* Two positives or two negatives may combine, but the chemical phenomena resulting from such combinations are usually slight, the compound partaking of a mechanical rather than of a chemical nature.

In affinity, moreover, we note a certain *elective power.* If, *e.g.*, hydrochloric acid be poured on lime and alumina, upon both of which it is capable of acting, we find that the acid acts by preference on the lime ("Elective Affinity" of Bergman).

(*β.*) *The particles concerned must be brought into absolute contact.*—This may be effected by various agencies, such as heat, solution, or mechanical action.

II.—The Phenomena of Affinity.

The phenomena of affinity are those indicative of change. With this change, however, no loss of matter occurs.

The resulting changes may be effected (1) by a direct combination of the elements or compounds; (2) by the displacement or mutual exchange of a group or element in one body by a group or element from another. To these must be added (3) a rearrangement of the atoms or groups of which a body is composed (molecular change), and (4) the more or less complete breaking up of the substance (decomposition), as illustrative of other changes that may occur in a chemical compound. But for the present we are mainly occupied with the first two results of the chemical force.

In *a mechanical mixture* the constituents are not changed, and consequently the nature of the compound is a mixture of the natures of the constituents. In *a chemical mixture* the properties of the resulting compound or compounds frequently bear no resemblance whatsoever to the properties of the constituents of which it or they are composed.

In all chemical combinations we must be prepared for more than one new substance being formed. If the body resulting from chemical union be a homogeneous gas, the residue, after diffusion, will have the same composition as the original gas, whereas, if it be a mixture, this will almost certainly not be the case, the lighter molecules passing through the diaphragm more rapidly than the heavier. (*See*

Diffusion, *Index.*) If it be a homogeneous liquid, its boiling point at given pressures will be constant from the first to the last drop. Thus fractional distillation is employed to separate mixed liquids. If it be a homogeneous solid, it will show itself in the constancy of the results of detailed analysis—in possessing the same specific gravity at like temperatures—in the uniformity of the shape and angular value of the crystals (always remembering the possibility of one substance having two or more shapes)—in the uniformity of the results of fractional crystallisation—in the constancy of the fusing point—in definite solubility at definite temperatures—and lastly in the consistency of the results of fractional solution.

Changes in the *sensible,* the *physiological,* the *physical,* and the *chemical* properties of bodies may be noted as the result of affinity.

(A.) Changes in the Sensible Properties.

(*a.*) *Color:* This may be—(1.) *Produced* (*e.g.*, if solutions of potassic iodide and plumbic acetate (both of which are colorless) be mixed, the yellow plumbic iodide is formed). (2.) *Altered* (*e.g.*, the action of an acid on litmus, or of an alkali on turmeric). (3.) *Destroyed* (*e.g.*, the action of chlorine on indigo).

(*β.*) *Odor:* This may be—1. *Produced* (*e.g.*, sulphuretted hydrogen, a compound of sulphur and hydrogen). (2.) *Altered* (*e.g.*, nitrobenzene, formed by the action of nitric acid on benzene). (3.) *Destroyed* (*e.g.*, action of chlorine on sulphuretted hydrogen).

(*γ.*) *Taste:* This may be—(1.) *Produced* (*e.g.*, nitrogen and hydrogen form ammonia). (2.) *Altered* (*e.g.*, chlorine and sodium form common salt). (3.) *Destroyed* (*e.g.*, baric oxide and sulphuric acid form the tasteless baric sulphate).

(B.) Changes in the Physiological Properties.

(*a.*) *Harmless bodies become active.*—For example, (1.) *Strychnia,* a deadly poison, is formed by the combination of the harmless elements, carbon, hydrogen, oxygen, and nitrogen. (2.) *Sulphuric acid,* a corrosive poison, is formed by the combination of the inert elements, sulphur, hydrogen, and oxygen.

(*β.*) *Active bodies become inert.*—Upon this depends the action of chemical antidotes. Thus, sulphuric acid is a poison, but if this be combined with calcic hydrate, the inert body calcic sulphate is formed.

(C.) Changes in the Physical Properties.

(*a.*) *Aggregation.*—Thus—(1.) Solids become liquids and gases. (2.) Liquids become solids and gases. (3.) Gases becomes solids and liquids.

(*β.*) *Density.*—The density of bodies is usually increased by affinity.

A change in other properties takes place as the result of altered density, such as the hardness of a body, its sonorousness, etc.

(γ.) *Thermotic properties.*

(i.) *Temperature.*—Heat always results from the play of affinity. The heat evolved may vary from an imperceptible rise of temperature to actual combustion. In those cases where cold is apparently produced, the chemical act is always accompanied by some change of state of the constituents, the heat required to effect the conversion of the solid to a liquid, or of the liquid to a gas, being in excess of the heat produced by the agency of the chemical force. (*See* THERMO-CHEMISTRY.)

(ii.) *Fusibility.*—With few exceptions the chemical compound is more fusible than the mean fusibility of the constituents.

(1.) *Fusibility increased.*—A mixture of 1 part of lead, 1 of tin, and 2 of bismuth, melts at 167° F. (75° C.), whereas the mean melting point of the constituents would be 512° F. (267° C.).

(2.) *Fusibility diminished.*—Such cases are rare. The metallic sulphides supply us, however, with illustrations.

(iii.) *Volatility.*—This may be increased or diminished.

(1.) *Volatility increased.*—When carbon (a non-volatile body) is combined with sulphur (volatile at 600° F., 316° C.), a liquid (carbonic disulphide) is formed, which requires an enormous cold even to render it viscid, and is volatile at ordinary temperatures, boiling at 111° F. (44° C.).

(2.) *Volatility diminished.*—Water boils at 212° F. (100° C.). In certain chemical compounds, however, it is practically non-volatile.

Again, the electrical states and the crystalline forms of bodies are altered by the play of affinity.

III.—Circumstances Influencing Chemical Affinity.

Inasmuch as affinity depends on molecular attraction, it follows that whatever tends, on the one hand, to bring the particles together, or on the other hand, to separate them, must influence the action of chemism, in the former case assisting, and in the latter interfering, with the activity of the force.

1. GRAVITATION MODIFIES CHEMICAL ACTION.

Gravity affects chemical action by the disposition of the heavier particles to sink, and of the lighter particles to rise to the surface.

2. COHESION MODIFIES CHEMICAL ACTION.

Affinity being a molecular force, it follows that it will be favoured by influences that lessen cohesion, such as mechanical division (powdering), heat (fluidity), or solution. The action of cohesion in influencing the force may be either exerted upon the constituents or upon the resultant :—

(*a.*) *Cohesion of the Constituents.*—Tinder burns readily, compact coke with difficulty. A lump of lead is very slowly acted upon when exposed to the air, but if the metal be in a finely powdered state (*pyrophoric*) it instantly ignites. If finely powdered antimony be sprinkled into chlorine it takes fire, but this intense chemical action does not occur when a lump of the metal is placed in the gas. Thus too, with a decreasing density of the carbon allotropes, we find an increase of combustibility.

(*β.*) *Cohesion of the Resultant.*—When sulphuric acid is added to a baric nitrate solution, baric sulphate is precipitated. The sulphuric acid thus removes the barium out of the sphere of chemical action, by reason of the superior cohesion of the resultant. This action was often attributed to what is called *superior affinity*, but there are difficulties in admitting this explanation. For, if acetic acid be added to a solution of potassic carbonate in *water*, carbonic anhydride escapes, and potassic acetate is formed ; but if carbonic anhydride be passed through a solution of potassic acetate in *spirit*, acetic acid is set free and potassic carbonate is formed, which, being insoluble in the spirit, is precipitated.

3. ELASTICITY (VOLATILITY) MODIFIES CHEMICAL ACTION.

The action of elasticity (that is, the absence of cohesion) upon affinity, is closely related to that of cohesion (that is, the absence of elasticity). Both are capable of effecting the removal of bodies from compounds—cohesion, by reason of the insolubility of certain bodies, and elasticity by reason of the volatility of others. But, although the action of cohesion and of elasticity are *analogous*, they are often *opposite*. If, for example, we add ammonia to a solution of magnesic sulphate, magnesia is precipitated, and ammonic sulphate remains in solution. This precipitation of magnesia is the action of *cohesion*. But if dry ammonic sulphate and dry magnesia are heated together, ammonia is expelled and magnesic sulphate is formed. This evolution of ammonia is the action of *elasticity*. It is the spring of repulsion between the particles, or, in other words, the distance maintained between the particles (elasticity), which prevents hydrogen and oxygen combining, but if this repulsion or distance be overcome by some such power as pressure, heat, or the action of spongy platinum, combination results. Thus elasticity is employed by the chemist both for the purpose of breaking up compounds and of producing new ones. Acids, bases, and salts are all more or less affected by its action ;—

(*a.*) *Acids.*—If an acid be added to a salt containing an acid capable either of assuming a gaseous form at ordinary temperatures, or of being converted into vapor at a temperature below that required to volatilise the acid added to displace it, the acid in the salt will be driven off and a new compound formed, consisting of the base of the original salt with the new acid. For example, if we add to a carbonate almost any acid, the carbonic anhydride of the salt is immediately evolved. Thus—

Potassic carbonate + sulphuric acid = potassic sulphate + carbonic anhydride.

Again : Sulphuric acid displaces nitric, hydrochloric, acetic, formic, butyric, and other volatile acids from their salts during distillation.

Further, it is to be noted that whatever tends to increase the elasticity of a body, such as heat, will also favour or modify chemical action. This circumstance explains certain contradictory phenomena, whereby salts of strong acids are decomposed by the action of weak acids. For example, sulphuric acid, we say, has a strong affinity, and boric acid a weak affinity for bases. If sulphuric acid be added to a solution of sodic borate, boric acid is set free, and sodic sulphate formed. But if sodic sulphate and boric acid be fused together, sulphuric acid is volatilised (elasticity) and sodic borate is formed. The same is also true of the action of silicic and phosphoric anhydrides on the sulphates. Or, again, if oxalic acid be boiled with a solution of a chloride, hydrochloric acid will be expelled from the solution. Thus a feeble acid may drive off a strong acid, provided the stronger acid be the more volatile of the two.

(β.) *Bases.*—If a salt of a volatile base be heated with a fixed base, the fixed base displaces the volatile base. For example, if an ammonic salt be heated with potassic hydrate, a salt of potash is produced, and ammonia gas evolved. Here, again, contradictory phenomena may be noted. For if ammonia be added to an aluminic sulphate solution, alumina is precipitated and ammonic sulphate is formed ; but if dry alumina and dry ammonic sulphate be heated together, ammonia is evolved and aluminic sulphate is formed.

(γ.) *Salts.*—Reactions of a similar nature occur in the case of salts. If a solution of ammonic carbonate be added to a solution of calcic chloride, calcic carbonate is precipitated and ammonic chloride remains in solution ; whilst, on the contrary, if dry ammonic chloride and dry calcic carbonate be heated together, ammonic carbonate is evolved and calcic chloride remains.

The power of elasticity on affinity is curiously influenced by certain mechanical processes, whereby the components of the body undergoing change are removed from the sphere of action. For example, if ferric oxide be heated in a current of hydrogen, the iron is reduced, the little steam formed being carried away by *the excess of hydrogen;* whilst if metallic iron be heated in a current of steam, the water is decomposed, ferric oxide is formed, and the hydrogen liberated is carried away by *the excess of steam.*

Further chemical action may be retarded if the escape of bodies be prevented by mechanical means. For example, if an acid be poured on calcic carbonate in a flask provided with a stopcock, the stopcock being open, carbonic anhydride escapes, owing to its elasticity, and a new lime salt with the acid is formed ; but if the escape of the carbonic anhydride be prevented by closing the stopcock, the formation of the new salt will be impeded, the action again proceeding when the stopcock is re-opened.

Again, if calcic carbonate (as in a lime kiln) be heated *exposed to the air,* all the carbonic acid will be driven off, and quick lime (CaO) remain. But if calcic carbonate be heated in a *closed* tube, so that the escape of the carbonic anhydride is prevented, it may be fused without decomposition resulting.

Again, if hydrate of chlorine be sealed up in a glass tube, it remains solid even at 68° F. (20° C.) the pressure of the chlorine stopping decomposition; but if it be exposed to air a few degrees above the freezing point of water, it liquefies with disengagement of chlorine. Similarly a hydrate of sulphuretted hydrogen may be preserved under pressure.

4. ADHESION MODIFIES CHEMICAL ACTION.

Just as cohesion opposes, so adhesion invariably assists affinity. Nor is this other than would be expected, when we remember the close relationship subsisting between affinity and adhesion—indeed, not unfrequently it is difficult to mark an exact dividing line. The powerful influence of solution (*i.e.*, the adhesion of liquids and solids or of liquids and gases) in aiding affinity, has been already referred to. Solution effects a minute subdivision of, and an increased freedom of motion amongst the molecules, thereby favouring contact of different molecules. As an example—baric nitrate is soluble in water as well as in *dilute* nitric acid, but is insoluble in *concentrated* nitric acid. If strong nitric acid be poured on baric carbonate, very little, if any, action results ; but if water be added to the mixture the action becomes energetic, carbonic anhydride is evolved, and baric nitrate remains in solution. The chemical action in this case did not occur until the circumstances favoured solution. So also an alcoholic solution of an acid (as tartaric acid) will not decompose a carbonate (as potassic carbonate), unless the resulting salt is soluble in alcohol. If dry sulphuretted hydrogen be mixed with dry sulphurous anhydride they do not re-act, whilst decomposition is immediate if moisture be present.

(A.) *Solution.*

Solution implies the admixture of a substance (solid, liquid or gaseous) with a solvent. It may be assumed that solids and gases become liquid when dissolved. The term "*miscibility*" is used to imply the solution of liquids, and "*absorption*" the solution of gases.

In dissolving a salt in water a contraction of volume (ammonic chloride being an exception) results, together with the development or the absorption of heat. The development of heat takes place when the solvent combines chemically with the substance acted on, as, *e.g.*, when KHO (potash) is mixed with water, KHO, $2H_2O$ is formed. The absorption of heat (cold) occurs either when no such chemical action takes place, or, at any rate, when the heat absorbed (latent) required to effect liquefaction exceeds the heat produced by the chemical act. Thus if KHO, $2H_2O$ be dissolved in water, cold results. The solution of a double salt produces a greater cold than the sum of the cold produced by the solution of the separate salts of which it is composed, because the heat given out by the union of the two salts has to be absorbed when the double salt is dissociated. All salts capable of dissolving in water, according to Guthrie, form definite solid compounds, having fixed fusing points with the solvent. To the compounds solid below 32° F. (0° C.) he has given the name cryohydrate. The fusing point of that cryohydrate formed at the lowest temperature (for the same salt often forms several cryohydrates) is the limit of cold attainable by a given freezing mixture, the maximum effect being produced when the ingredients are rightly proportioned to form this cryohydrate.

(I.) *The Action of Acids on Salts in solution.*

(*a.*) If an acid be added to a solution of a salt, such acid being of nearly equal chemical power to the acid of the salt, and with the base of which salt it can unite to form a soluble compound, the probability is that the base will be divided between the two acids, equally or unequally, both acids being also present in solution in a free state.

Example: Sulphuric acid + potassic nitrate = potassic sulphate + potassic nitrate + sulphuric acid + nitric acid.

Thomsen has shown that in a solution of equal equivalents of two acids with a quantity of base only sufficient for the neutralization of one, the base is commonly appropriated by that acid with which it forms the least heat on neutralization, a fact opposed to Berthelot's views of maximum work.

(*b.*) If an acid be added to a solution of a salt, such acid being of much greater chemical activity than the acid of the salt, but with the base of which salt it can unite to form a soluble compound, the strong acid will then appropriate the whole of the base, and set free the whole of the acid originally combined with the salt.

Example: Sulphuric acid + sodic borate = sodic sulphate + boric acid.

(*c.*) If an acid be added to a solution of a salt, aqueous or otherwise, it being immaterial whether the acid so added be of greater or of less chemical power than the acid already present in the salt, but with the base of which salt it is capable of forming a precipitate insoluble in the menstruum in which the salt is dissolved; the acid added will appropriate the whole of the base, and set free the original acid.

Examples (1) Sulphuric acid + baric nitrate = baric sulphate + nitric acid.
(2) Hydrocyanic acid + argentic nitrate = argentic cyanide + nitric acid.
(3) Tartaric acid + argentic sulphate = argentic tartrate + sulphuric acid.

(*d.*) If to a solution of a salt, the acid of which is insoluble in the menstruum in which the salt is dissolved, an acid be added which forms with the base of the salt a soluble salt, the acid added will then combine with the whole of the base, whilst the acid previously in combination with it will be precipitated.

Example: Nitric acid + potassic tungstate = potassic nitrate + tungstic acid.

(II.) *The Action of Bases on Salts in solution.*

(*a.*) If to a solution of a salt, the base of which is soluble, another base be added which is also soluble and capable of forming a soluble salt with the acid of the original salt, the acid will then be divided between the two bases in proportion to its affinity for each.

Example: Potassic hydrate + sodic nitrate = sodic nitrate + potassic nitrate + sodic hydrate + potassic hydrate.

Note further that in some cases a portion of the base may be precipitated, owing to its imperfect solubility.

Example: Potassic hydrate + baric nitrate = potassic nitrate + baric nitrate + potassic hydrate + baric hydrate (a portion of which will be precipitated).

(*b.*) If to a solution of a salt, the base of which salt is entirely insoluble, a base be added which forms a soluble salt with the acid of the original salt, then the base of the original salt will be precipitated, and the whole of the acid set free will combine with the new base.

Example: Ammonia + ferric sulphate = ferric oxide + ammonic sulphate.

This rule has its exceptions. Thus ammonia will not throw down the base of mercuric cyanide, although it is insoluble.

(*c.*) If to a solution of a salt a base be added, with which the acid of the salt forms an insoluble compound, all the acid of the original salt will be precipitated with the newly added base, the other base if soluble remaining in solution.

Example: Baric hydrate + potassic sulphate = baric sulphate + potassic hydrate.

(*d.*) If to a solution of a salt, the base of which is insoluble, a base be added which forms an insoluble compound with the acid of the original salt, both bases, as well as the acid previously in contact with the one base, will be precipitated from the solution.

Example: Baric hydrate + argentic sulphate = baric sulphate + argentic hydrate.

(III.) *The Action of Salts on Salts in solution.*

(*a.*) If a soluble salt be added to a soluble salt, both salts, by a mutual interchange of acids and bases also forming soluble salts, a solution of four salts in unknown proportions will probably result.

Example: Potassic sulphate + sodic nitrate = potassic sulphate + potassic nitrate + sodic sulphate + sodic nitrate.

(*b.*) If a soluble salt be added to a soluble salt, both salts by a mutual interchange of acids and bases forming an insoluble or sparingly soluble salt, decomposition will result, the least soluble compound being precipitated.

Example: Argentic nitrate + sodic chloride = argentic chloride + sodic nitrate (the argentic chloride being precipitated).

(B.) *Adhesion of Gases to Solids* (*Surface action*).

If a piece of porous charcoal be placed in ammonia gas standing over mercury, the charcoal, by reason of the force of adhesion, condenses the gas within its pores. Again, if a piece of charcoal be saturated with hydrogen by being employed as a negative electrode in decomposing water, the charcoal will, in that condition of saturation, decompose a solution of sulphate of copper or of nitrate of silver, the metal being deposited on the charcoal. Here carbon and condensed hydrogen act as a voltaic circuit, the hydrogen playing the part of the oxidisable metal, and the charcoal of the conducting plate.

The action of spongy platinum in effecting the combination of mixed hydrogen and oxygen gases, and the ease with which a piece of platinum foil may be kept red hot by allowing a jet of hydrogen or of coal gas to play upon it (Dobereiner's lamp), are further illustrations of the power of adhesion upon affinity. It is *the elastic force* of the gases that prevents the union of hydrogen and oxygen. The platinum, however, by effecting a condensation of the gases upon its surface, brings them within the range of each other's chemical attraction (Faraday). It follows that the larger the surface exposed, the greater will be the condensation. Hence the greater activity of finely divided platinum (platinum black). In this power of adhesion, moreover, we have the means of effecting unusual chemical combinations. For example, spongy platinum will coerce the formation of water and nitric acid from ammonia and air, a reaction impossible to effect by heat alone ($NH_3+2O_2=HNO_3+H_2O$)—whilst ammonia may be formed from a mixture of the oxides of nitrogen and hydrogen in a similar manner ($N_2O_2+5H_2=2NH_3+2H_2O$). Sulphurous anhydride may be oxidised by the action of spongy platinum to sulphuric anhydride, a process once suggested as a method for preparing sulphuric acid. So, again, methylamine may be formed from an admixture of hydrogen and hydrocyanic acid—ammonic carbonate from a mixture of ethylene and nitric oxide, &c. Nor is this action peculiar to platinum. In an inferior degree gold, silver, palladium, iridium and such other metals as possess no strong affinity for oxygen (otherwise the surface of the metal would soon become oxidised), as well as inert bodies, such as pounded glass, porcelain, &c., act similarly. This action of surface is modified and often stopped by the presence of minute quantities of certain vapours and gases, such as carbonic oxide, carbon disulphide, phosphoretted hydrogen, sulphuretted hydrogen, etc.

(C.) *Action of Nascent Matter.*

If hydrogen be generated in the presence of arsenious acid, it combines with the arsenicum to form arseniuretted hydrogen (AsH_3). But its power of combining with the arsenicum is limited to the moment at which it is generated. For, if the hydrogen be conveyed through a solution of arsenious acid, no such combination results. Again, if hydrogen be passed through a mixture of argentic chloride and water, no action on the silver salt occurs ; but if the hydrogen be generated *in the presence* of argentic chloride, the silver will be reduced.

Again, in the colour tests for strychnia, aniline, &c., it is essential that the oxygen be generated in the presence of these bodies. This is commonly effected by the action of sulphuric acid on some salt, such as potassic bichromate, &c. The oxygen, as Letheby showed, liberated at the positive pole of the battery, may be employed. But by whatever means we set free the oxygen, it is essential that the gas be *nascent*, that is, that the bodies upon which it is to act should be present at the moment of its birth.

We may suppose in such condition that the gases are for the moment under coercion, in other words, that the elasticity of the gases has not yet come into play.

5. Influence of Mass (or Quantity) on Affinity.

It will be remarked, that if one body unites with another body in several proportions, the compound which possesses the smallest number of elements is generally the most difficult to decompose. For example, if plumbic dioxide (PbO_2) be heated, plumbic oxide (PbO) and oxygen are formed, but if the same heat be continued, it will be found insufficient to decompose the plumbic oxide.

We have now to examine this subject from another point of view.

If we add an equivalent of sulphuric acid to a solution of potassic nitrate, we have said that a mixture of potassic sulphate and potassic nitrate will be formed, together with free acids. Suppose we add, however, *a great excess* of sulphuric acid, the question is, Will this excess influence the relative quantities of the two salts formed ? This subject was first investigated by Berthollet, who deduced the law "*that in elective attraction the power exerted is not in the ratio of the affinity simply, but in the ratio compounded of the force of affinity and the quantity* *of the agent.*" That is, in other words, that quantity may be made to compensate for a weaker chemical action. Gladstone (*Phil. Trans.*, 1885, p. 179) has further investigated this subject, employing the change of color effected by different mixtures, *e.g.*, by the action of potassic sulphocyanide on ferric salts, as a means of determining the extent of the decomposition. The fact was demonstrated that if a solution of potassic sulphocyanide be mixed with a solution of a ferric salt, the quantity of sulphocyanogen of the former being exactly equivalent to the iron of the latter, the whole of the iron was not converted into ferric sulphocyanide; for if a second equivalent of potassic sulphocyanide be added, more ferric sulphocyanide was formed (proved by increased depth of colour), and so on with a third and a fourth equivalent, up to 375 equivalents; although the effect of every addition became less and less. Gladstone concludes that mutual interchange takes place in determinate proportions, *independent* of the combination of the compounds, but *dependent* on the mutual strength of their affinities and on the proportions (or mass) of each constituent present.

The effects of quantity in the combinations of gases, have also been investigated by Bunsen and Debus, and more recently by Meyer and by Harcourt and Essen. Mixtures of hydrogen, oxygen, and carbonic oxide, in various proportions, the hydrogen and carbonic oxide being always in excess, were fired, and the relative proportions of water and carbonic anhydride formed were estimated. These were found to be dependent on the preponderance of the carbonic oxide, in accordance with an ascertained law.

6. Mechanical Force may modify Chemical Action.

Pressure, percussion, friction, agitation, and indeed all forms of mechanical action influence the chemical force, both disturbing and favouring its manifestation. A solution of tartaric acid added to a solution of potassic chloride needs to be well stirred in order to secure the complete formation of the potassic tartrate. This, as well as numerous other cases, where the stirring-rod is so constantly in requisition in the laboratory, illustrates the influence of mechanical action on affinity.

On the other hand, mechanical action may destroy the force. For example, a touch disturbs the equilibrium of the particles of iodide of nitrogen.

7. Contact Decomposition.—Concurring Attractions.—Ferments.—Catalysis.

Certain bodies exert on other bodies by mere contact (*i.e.*, by their presence) a power, whereby the decomposition of the body is effected, and new compounds are formed. The substance which excites this action appears neither to give anything to, nor to take anything away from the compound on which it acts.

Illustrations of contact decomposition may be noted in the following cases :—

(1.) Hydric peroxide (H_2O_2) is a powerful oxidising agent. If, however, finely divided metallic gold, silver, or platinum be added to the liquid, it suffers decomposition, although the metal itself will undergo no change. Further, if instead of employing metallic gold or silver, oxide of gold or oxide of silver be placed in the liquid, not only will the hydric peroxide be decomposed, but the metallic oxide itself will suffer decomposition and the metal be reduced.

(2.) Again, potassic chlorate is decomposed at 698° F. (370° C.), liberating oxygen. If, however, the potassic chlorate be mixed with manganese dioxide or with cupric oxide, and heated, the oxygen will be given off at a temperature of from 446° to 500° F. (230° to 360° C.), although the manganese dioxide apparently undergoes no change. (*See* OXYGEN.)

(3.) If air and hydrochloric acid be passed over hot bricks impregnated with cuprous chloride or cupric sulphate, the formation of chlorine from the decomposition of the HCl takes place far more completely than it would in the absence of the copper salt. The copper salt apparently, however, undergoes no change and does not require renewal. (*See* CHLORINE.)

(4.) Nitric acid converts starch into oxalic acid ($H_2C_2O_4$), but in the presence of a manganese salt, carbonic anhydride and not oxalic acid is formed.

(5.) *Sugar,* under the influence of yeast, breaks up into alcohol and carbonic anhydride, the yeast apparently neither giving anything to, nor taking anything from, the sugar.

(6.) *Starch* in the presence of diastase is converted into sugar, an action taking place in every germinating seed.

(7.) *Amygdaline* in the presence of synaptase (an albuminoid principle present in the pulp of the seed) breaks up into hydrocyanic acid, oil of bitter almonds, sugar, and formic acid.

These last three illustrations are regarded as cases of fermentation. Although the bodies capable of effecting the change (ferments) appear in no way to contribute to the new products, they undergo certain specific changes during the process.

The theories to account for these phenomena will be discussed under fermentation. Berzelius imagined them due to a new force, which he termed *Catalysis.* Catalysis means fermentation, and the explanation of Berzelius is little else than "that fermentation is fermentation." Liebig suggested that the motion taking place in the atoms of one body were communicated to the atoms of another body, setting up similar changes, just as one body on fire is able to set on fire other bodies. Very frequently, however, the body that starts the fermentation, and the body that ferments undergo vastly different changes. In such cases as 1, 2, 3 and 4 given above ("*concurring attractions*"), the catalytic body, as it has been called, probably plays some definite part as a go-between. In Case 1, Brodie has shown that there is a direct relationship between the quantity of metallic oxide reduced and the hydric peroxide decomposed, and he supposed that particles of the same element may attract one another from the atoms being in different electrical states. In Case 2, the cupric chloride is being constantly formed and unformed, the apparently continuous action being a series of separate reactions. Liebig considered that various zymotic diseases were due to the contact of germinal matter (acting as a ferment) with substances in the blood capable of undergoing fermentation. The materials in the blood capable of being thus split up having been exhausted, the disease could not, he explained, recur.

It is worth noting that bodies formed with absorption of heat, are peculiarly sensitive to the action of catalytic agents.

8. INFLUENCE OF HEAT AND COLD ON AFFINITY.—THERMO-CHEMISTRY.

The chemical force acts only within a given range of temperature, the limits of action varying with different bodies. A red-hot glass rod, *e.g.*, will effect the combination of oxygen and hydrogen, whilst, as Grove has shown, a white heat is necessary to decompose the water-gas formed into oxygen and hydrogen (*Phil. Trans.*, 1847). Mercury, which is unacted upon by oxygen at common temperatures, forms mercuric oxide (HgO) at 698° F. (370° C.), whilst mercuric oxide at a still higher temperature is again resolved into mercury and oxygen. Baric oxide (BaO) at a *red heat* becomes baric peroxide (BaO_2), whilst at a *white heat* the baric peroxide is resolved into oxygen and baric oxide (BaO). Possibly the range of temperature within which bodies can act is a limited one, but, at any rate, it is evident that in many cases a high temperature will undo the work effected at a lower temperature.

(*a.*) *Heat may promote affinity.*—It does so by overcoming the force of cohesion. Thus the cold produced by a bath of ether and solid carbonic anhydride (—104·8° F., or —76° C.) prevents the combination of iodine and phosphorus, or of chlorine and finely-powdered antimony, but these bodies severally combine on being again exposed to ordinary temperature. At common temperatures, again, sulphur will not combine with carbon, whilst at 500° F. (260° C.) their union may be easily effected.

(*β.*) *Heat may destroy affinity.*—It does so by effecting a separation of, and giving greater mobility to, the ultimate particles of the body. Probably, indeed, all substances might be decomposed if we could apply sufficient heat. At a red heat, C_2H_4 is decomposed into carbon and CH_4, whilst at a higher temperature CH_4 is further decomposed into hydrogen and carbon. Again, if steam and carbonic anhydride be passed through a red-hot porcelain tube, the gases left after the un-decomposed carbonic anhydride has been absorbed by potash will be found to be an explosive mixture of oxygen, hydrogen, and carbonic oxide, the hydrogen of the steam at the moment of its liberation from the oxygen, reducing a portion of the carbonic anhydride. Even the partial reduction of unmixed carbonic anhydride alone into carbonic oxide and oxygen may be effected by passing it through a porcelain tube heated to 2372° F. (1300° C.). Again, carbonic oxide may be partially resolved into carbon and carbonic anhydride by passing it through a heated porcelain tube, in the axis of which is placed a small and hollow brass tube (kept cool by a constant current of water within), upon which the carbon may be deposited. In a similar manner sulphurous anhydride may be partially resolved into sulphuric anhydride and sulphur. And the fact must be noted, that an absorption of heat corresponding to the force required to overcome the chemical attraction of the elements always occurs.

To the *partial* decomposition of bodies at a high temperature Deville has given the name "*dissociation*." Examples in the case of NH_4Cl, PCl_5, and $(NH_3)_2CO_2$ are mentioned under "Abnormal vapour densities." (Page 45.)

In dissociation, as distinct from ordinary decomposition, the products have a tendency to recombine and form the original compound. Further, the volatile dissociated products have a tension, *i.e.*, a pressure, constant for each temperature, and dependent on temperature only.

(γ.) *Heat modifies chemical action.*—In other words, the nature of the products may be influenced by the temperature. Thus, carbonic anhydride and water are formed by the combustion of ether in air, and carbonic anhydride and nitrogen by the combustion of cyanogen. But if a platinum wire be allowed to glow in a mixture of air and ether, aldehyde and acetic acid will be formed, whilst if the glowing platinum wire be placed in a mixture of cyanogen and oxygen, nitric oxide, and not nitrogen, will be produced.

A depression of temperature commonly diminishes chemical action. Dewar has shown that there is no action between potassium and liquid oxygen, whilst frozen zinc ethyl does not ignite in liquid oxygen. Neither phosphorus nor antimony fire in chlorine when both are cooled to —105° F. (—76·1 C.). Similarly cold prevents the action of alcohol on chlorochromic acid, of ammonia on chlorine, of iodine on phosphorus, &c.

THERMO-CHEMISTRY.

Every chemical act, then, is accompanied by the development or the absorption of heat. The heat developed in any chemical action is the exact measure of the chemical action, *provided* that at the same time there be no manifestation of any other force such as electricity, light, alteration of physical state (*e.g.*, fluidity), etc.

To Thomsen of Copenhagen, Favre, Berthelot, and others, we are indebted for many researches on thermal equivalents. These determinations have been made either—

(1.) From the heat developed by combining bodies; or

(2.) From the heat absorbed in decomposing them.

The heat absorbed by decomposing a substance into its original constituents, is equivalent to the heat developed on combining them.

I. *The heat developed by combining bodies.*—Of this a simple case may be cited: Hydrogen, chlorine, and the product of their combination (hydrochloric acid) are gases, *i.e.*, both elements and product are in the same physical state. A platinum vessel filled with hydrogen, is immersed in a calorimeter; a chlorine jet is burnt in the hydrogen, and the HCl formed conveyed through the water of the calorimeter. The experiment finished, the amount of HCl is estimated, and the increased temperature of the water noted. Thomsen, by this means, estimated the heat developed in the formation of a molecule of HCl (36·5 grams) as 22,000 thermal units.

We need scarcely point out that numerous experimental details have to be observed to ensure accuracy, *e.g.*, that the gases should have the same temperature as the water in the calorimeter; that the heat-capacity of the whole apparatus should be known, etc.

Supposing the same experiment be made with oxygen and hydrogen, we should find that 68,357 thermal units were developed for each molecule (18 grams) of H_2O formed. But here a new difficulty arises, viz., that the aqueous vapour has been liquefied;—in other words, that the product is not in the same physical state as the elements from which it was formed. Hence the heat developed results from the combination of H_2 and O, modified by the change of state.

Again, it will be manifest that great difficulties beset researches on the thermic results of the union of carbon and hydrogen, because we know nothing for certain either of the latent heat of carbon vapour, or of the exact differences of heat developed by the several allotropic forms of carbon. As regards the latent heat of carbon vapour, experiments indicate the necessity for an expenditure of a large amount of force (by one calculation of 67,840 units) to convert it from a passive into an active form capable of chemical union, whilst with respect to the different allotropes, it has been shown that whilst wood charcoal in passing into CO_2 develops 96,960 thermal units, graphite only develops 93,600.

II. *The heat absorbed by decomposing bodies.* — The alternative naturally occurred :—Supposing it be not possible to estimate the heat developed in forming a body, can the heat absorbed by its decomposition be determined ?

This has been done in certain instances, as, *e.g.*, in the case of ammonia. When chlorine is passed into a dilute solution of ammonia (using a slight excess) ammonic chloride is formed, and nitrogen set free ($4NH_3 + 3Cl = 3NH_4Cl + N$). Here one molecule of NH_3 is decomposed by 3 atoms of Cl. The calorimeter shows that 119,613 thermal units are rendered sensible by the reaction of 3 atoms of chlorine (= 106·5 grams) on 4 molecules of ammonia (= 68 grams) *in the presence of water.*

Numerous experiments to supply accurate data for correction were demanded in this experiment. Thus, it was necessary to know, (1) the heat developed by the union of chlorine and hydrogen in the presence of water (= 39,315 units) ; (2) the heat developed by the union of ammonia and hydrochloric acid in the presence of water (= 12,270 units) ; (3) the heat absorbed by the decomposition of the ammonia ; and (4) the heat of the absorption of ammonia by water. Corrections being made for these, the thermal equivalent corresponding to the formation of an ammonia molecule (= 17 grams) was found to be 26,707 thermal units.

The quantity of heat liberated in any reaction is a measure of the sum of the chemical and physical work performed. This follows naturally on the well-known law of the conservation of energy. But Berthelot has enunciated a further law, known as the "*law of maximum work*," which declares that every chemical change accomplished without the intervention of foreign energy tends to the production of that body in the formation of which most heat is liberated. Thus, whilst hydrogen in combining with oxygen to form water (H_2O) yields 69,000 thermal units, it yields in combining with oxygen to form peroxide of hydrogen (H_2O_2) only 47,000 units. Hence given oxygen and hydrogen, water, and not peroxide of hydrogen, should be formed, whilst peroxide of hydrogen (which if formed from water must be by the intervention of some foreign energy, and the action be accompanied by the absorption of heat) should have a tendency to split up into water and oxygen. Similarly, N_2O_4 (34,000), rather than N_2O_3 (20,000), should be formed when N_2O is acted upon by an excess of oxygen.

Hence, if the question be asked, Will oxygen, in combining with any given body, form a high or a low oxide ? the answer is, It will be that oxide in the formation of which the greatest liberation of heat occurs.

Important results turn on the question whether absorption or liberation of heat has occurred in the formation of a compound. Given a compound formed directly, the formative action being accompanied by the liberation of heat, spontaneous decomposition of that body is not to be expected, some external power, such as electricity or heat, being needed to effect the change. But given a body where heat is absorbed during formation, then either spontaneous decomposition (as in the case of chloride of nitrogen), or readiness to enter into direct combination, or some other change accompanied by the liberation of heat, will be its probable characteristic.

And this same law of maximum work finds further confirmation in the case of substitution and of double decomposition. Thus chlorine decomposes bromides, and bromine decomposes iodides, because chlorine in combining with metals liberates more heat than bromine, and bromine more heat than iodine. Or one acid expels another from its salts when more heat is liberated by the union of the new acid with the same base, than the acid already in contact with it. But in all these cases there are many circumstances that may reverse the result, of which the chief is the alteration of physical state, and of the exertion by the medium of solution of any special solvent power on the product. Further, the law of maximum work does not hold good (indeed most often, as Thomsen has shown, the reverse is true) in the case of the neutralisation of acids and bases, the heat of neutralisation being independent of affinity, and dependent on the changes (expansion or contraction) that occur in the aggregation of the solution.

9. INFLUENCE OF LIGHT ON AFFINITY.

Light both promotes and destroys chemical action :—

(*a.*) *Light promotes chemical action.*—Thus, chlorine and hydrogen will not unite in the dark, but in direct sunlight they combine with explosion. Chlorine and carbonic oxide under the influence of light combine to form phosgene (light-formed) gas.

(*β.*) *Light destroys chemical compounds.*—Photography depends on the power of light to decompose silver compounds. Sunlight again decomposes nitric acid, oxygen being evolved, whilst the nitrous acid formed communicates a yellow tint to the acid.

10. INFLUENCE OF ELECTRICITY ON CHEMICAL ACTION (ELECTROLYSIS).

Electricity promotes and destroys chemical combination. Davy decomposed the alkalies by electricity, and by this means obtained the alkaline metals.

The decomposition of bodies by the electric current is termed *electrolysis.* It is not to be confounded with decomposition resulting from the passage of the electric spark, the action of which in such case is solely its heating property. The body electrolysed is called an *electrolyte.* The terminals of the battery used for the decomposition of the electrolyte (which are usually constructed of platinum, but may be of other material) are called *electrodes.*

To constitute a body an electrolyte, three conditions are necessary :—

(1.) It must be a compound body.

(2.) It must be a liquid (*i.e.*, either capable of being fused or of being dissolved).

(3.) It must, when in the liquid condition, be a conductor of the electric current.

The electric current being passed through the electrolyte, it is to be noted :—

(1.) That the compound body is broken up into two constituents (ions).

(2.) That these constituents are set free on the opposing surfaces of the two electrodes, and not in the intervening liquid.

(3.) That a certain class of bodies, called electro-negatives, uniformly appear at the positive electrode, *i.e.*, the pole attached to the platinum or carbon of the battery (*e.g.*, oxygen, chlorine, bromine, iodine, acids, etc.), whilst another class, called electro-positives, as uniformly appear on the negative electrode, *i.e.*, the pole connected with the zinc of the battery (*e.g.*, hydrogen and the metals).

Two important facts must be noted with reference to the quantity of electricity in relation to the work done :—

(1.) The quantity of electricity passing through an electrolyte is directly proportional to the quantity of the electrolyte decomposed.

(2.) The quantity of electricity required to decompose a compound molecule, is that quantity the compound molecule evolves when formed in the generating cell of the battery.

The question now arises, What is this quantity ?

This was the subject of Faraday's early researches, and, as the result, he enunciated the law of electro-chemical equivalents, which may be expressed as follows :—The quantities of the several elements eliminated from various electrolytes by similar amounts of electrical current are chemically equivalent. Thus, for every 1 by weight of hydrogen set free by x quantity of electricity, 8 by weight of oxygen and 35·5 of chlorine are set free by the same x quantity. To Faraday these numbers were the *equivalents* of the elements. By equivalents he implied, not the atomic weights (as the later chemists assumed) but, the relative weights of the elements (hydrogen being taken as unity) eliminated by electrolysis.

Modern chemists have added somewhat to these researches, although it must be admitted much depends on altered phraseology. All decomposable compound molecules of the same active atomicity require the same amount of electricity to decompose them. Thus the molecular weight of hydrochloric acid (HCl) is 36·5, and of argentic chloride ($AgCl$) 143·5. In both the active atomicity of the electro-positive element is 1. The amount of electricity that would decompose 36·5 grains of HCl would decompose 143·5 grains of $AgCl$.

But in cupric chloride ($Cu'' Cl_2=134{\cdot}2$) the copper is combined with two of chlorine, and is of dyad atomicity. The amount of electricity that would decompose 143·5 grains of chloride of silver would decompose $\frac{134{\cdot}2}{2} = 67{\cdot}1$ grains of chloride of copper.

Or, supposing the chlorides of silver and copper be mixed together in a single solution and electrolysed, by the time that 143·5 grains of chloride of silver were decomposed, 67·1 grains only of chloride of copper would be decomposed.

In other words, the quantity of metal deposited from compounds by a given quantity of electricity may be relatively determined by dividing the atomic proportion of the metal in the compound by its active atomicity. Thus, taking $Cu''Cl_2$ and Cu'_2Cl_2, the quantity of electricity that would deposit 31·6 grains of copper from the $CuCl_2$ would deposit 63·2 grains from the Cu_2Cl_2.

By the term "*secondary action*" is implied the chemical action of the primary products of decomposition, either (1) on the electrode, or (2) on the electrolyte, or (3) on the solvent employed. Thus—

(1.) If you electrolyse acidulated water with copper electrodes, the acid set free at the positive electrode would combine and form sulphate of copper with the copper of the electrode.

(2.) If you electrolyse a solution of chloride of sodium, you get (not chlorine and sodium, but) chlorine and hydrogen set free, because the sodium primarily formed, decomposes the water (forming $NaHO$), hydrogen being thereby liberated.

The secondary, or storage battery consists of two lead plates coated with lead sulphate and immersed in dilute sulphuric acid.

On passing an electric current through them, the positive plate becomes coated with PbO_2 (from the action of nascent oxygen on the sulphate), whilst the negative plate becomes coated with spongy metallic lead (from the action of nascent hydrogen on the sulphate). In this condition, and so long as the plates are kept separate, the energy remains stored. Connect the plates, a powerful current flows from the positive to the negative plate, both returning to their original condition, ready to be recharged by a primary electric current.

11. INFLUENCE OF VITAL FORCE ON CHEMICAL ACTION.

This influence is manifest in every living organism, from the production of a simple cell to the highest manifestations of life. Elements are re-arranged under the influence of life to form the constituents of the organism, and out of a single fluid all the elements of growth and nutrition are elaborated, whilst the various secretions (mucus, bile, urine, milk, etc.), have their compositions determined by the agency of the vital force.

Thus it would seem that all forms of force influence affinity. The influence depends on their power respectively either to draw particles nearer together, thus promoting affinity, or to separate them, thus retarding or preventing it.

IV.—Degree, Force, or Energy of Affinity.

There is great inequality in the action of affinity. The absence of energy between oxygen and fluorine, and the intensity of energy between oxygen and potassium, is an illustration. The more opposite the bodies on which affinity is brought to bear, the more intense is its energy.

Can we estimate, then, the amount of affinity between different bodies ? The attempts to express the amount of chemical action numerically, forms an interesting chapter in the history of chemistry.

1. Affinity Measured by Reference to the Specific Gravity of Bodies (Laplace and others).

The following table is from Laplace :—

Acetic acid (Sp. Gr. 1·063)	poured on	carbonates	displaces	carbonic acid.
Hydrochloric acid (Sp. Gr. 1·247)	,,	acetates	,,	acetic acid.
Nitric acid (Sp. Gr. 1·421) ..	,,	chlorides	,,	hydrochloric acid.
Sulphuric acid (Sp. Gr. 1·60) ..	,,	nitrates	,,	nitric acid.

Laplace argued that the greater the specific gravity of the acid, the more intense was its chemical action. But it was shown that in the case of other bodies their energy of action is almost in an inverse order to their specific gravity. Thus—

Baryta	5·456
Magnesia	3·60
Lime	3·180
Potash	2·20
Soda	2·13
Ammonia solution	0·90

It is manifest that specific gravity affords no test either of the absolute or relative power of the chemical force.

2. Affinity Measured by the Force of Adhesion (Guyton Morveau).

Guyton Morveau, who first suggested adhesion as a test of the energy of affinity, acted under the impression that adhesion was the first stage of affinity. He employed equal-sized discs of different metals suspended from one end of a scale beam, and estimated the weight necessary to separate them respectively from a layer of mercury. These weights he regarded as the measure of their affinity.

Affinity Measured by Adhesion (Guyton Morveau).

Gold	adheres to	Mercury with	a force of	446	grains.
Silver	,,	,,	,,	429	,,
Tin	,,	,,	,,	418	,,
Lead	,,	,,	,,	397	,,
Bismuth	,,	,,	,,	372	,,
Platinum	,,	,,	,,	282	,,
Zinc	,,	,,	,,	204	,,
Copper	,,	,,	,,	142	,,
Antimony	,,	,,	,,	126	,,
Iron	,,	,,	,,	115	,,
Cobalt	,,	,,	,,	8	,,

Achard followed out the same principle in greater detail, by using other solids and fluids. Gay Lussac estimated the force required to separate a circular glass disc (4·6 in. diameter) from the following fluids, and founds it as follows :—

From water ... (Sp. Gr. 1·000)—814·7 grains.
,, turpentine (Sp. Gr. 0·869)—523·6 ,,
,, alcohol ... (Sp. Gr. 0·819)—474·4 ,,

But there were manifest objections to these as tests of affinity :—

(1.) It was not a measure of affinity at all, but of adhesion.

(2.) It was more often a measure of cohesion than of adhesion, a layer of mercury being separated from mercury, or water from water, etc.

(3.) The results obtained as the energy of adhesion were often found to be exactly opposite to the energy of affinity.

3. Affinity Measured by the Amount of Force required to effect the Decomposition of a Compound.

(*a.*) *This decomposition may be effected by the agency of heat* (Fourcroy, Lavoisier, etc.).—A very slight heat, for example, is sufficient to destroy the combination of oxygen with certain metals, such as gold or silver, whilst no heat will effect the decomposition of certain other metallic oxides. Thus it is evident that the force between oxygen and calcium, for example, is very much greater than that between oxygen and gold.

An attempt was made in certain cases to express this amount in figures, *e.g.*, in the case of the sulphides, by noting the temperature at which they were decomposed, and deducting therefrom the temperature at which sulphur itself is volatile. Thus, sulphur volatilises at 836° F., whilst sulphide of iron (FeS_2) is decomposed at 1500° F. Therefore, $1500 - 836 = 664$, the amount of the force between sulphur and iron. Sulphide of gold (Au_2S_3) is decomposed at 842° F. ; $842 - 836 = 6$. Therefore, supposing the power of affinity holding the sulphur to the gold to be 6, in the case of iron it was regarded as 664 ; in other words, that the affinity between sulphur and iron was about 111 times greater than between sulphur and gold.

The principle of the conservation of energy clearly indicates, however, that given the absence of manifestation of any other force—*e.g.*, light, electricity, change of physical condition, etc.—the heat developed during the chemical act must be the true measure of the chemical action. Physical complications, however, have seriously interfered with accurate determinations. (*See* THERMO-CHEMISTRY, page 16.)

(*β*.) *The decomposition may be effected by the agency of a superior affinity.*—Mayow in 1674, Geoffry in 1718, and Bergman in 1775, attempted to estimate the force by what they called *single elective affinity;* that is, where one substance takes away another to the exclusion of a third. Thus, *ammonia* displaces magnesia from magnesic sulphate ; *soda*, ammonia from ammonic sulphate ; *potash*, soda from sodic sulphate ; *strontia*, potash from potassic sulphate ; and *baryta*, strontia from strontic sulphate. These experiments led Geoffry to invent tables of attraction, as they were called, of which the following is an illustration :—

TABLE OF ATTRACTION (Geoffry).

Sulphuric Acid.	*Potash.*
Baryta.	Sulphuric acid.
Strontia.	Nitric acid.
Potash.	Muriatic acid.
Soda.	Acetic acid.
Lime.	Carbonic acid.
Ammonia.	
Magnesia.	

These views held their ground until 1803, when Berthollet pointed out, as the result of a more rigid analysis of the question, the error into which Geoffry and Bergman had fallen, in overlooking the modifying effects of cohesion and elasticity. Further, he showed that Bergman's tables were simply tables of the order of decomposition, and not tables of the attractive force. Berthollet, however, fell into the opposite error of denying the existence of a superior attractive force in any sense, and of supposing that decompositions were always determined by cohesion and elasticity.

We should note, however, that Bergman was clearly aware of some influence other than affinity, affecting chemical results. This is shown by the fact, that in many cases he compiled two sets of tables, setting forth the different effects resulting from the combination of bodies by solution and by fusion respectively.

Guyton Morveau, seeing that no dependence could be placed on the measure of chemical action, as deduced from Geoffry and Bergman's tables of "*single elective affinity*," attempted to estimate the force by "*double elective affinity*," that is, where four elements are employed in the decomposition, the two of the one compound reciprocally acting on the two of the other. But still the same modifying influences were at work, and we may conclude with Berthollet that, whilst the tables of affinity give us good ideas of the order of decomposition, they are not, owing to the influence exerted by cohesion and elasticity, indications of the relative force of affinity.

4. Affinity measured by the Time of Combination.

It was suggested by Wenzel that the time required for solution might serve as a measure of affinity.

Thus he immersed known weights of different metals in a weak acid, and, at the end of a given time, estimated the quantity of the several metals dissolved. These quantities he supposed corresponded to the ratio of their affinities for the liquid in which they were placed.

Again, it will be noted that the energy of combination will be largely dependent upon the *cohesion* of the body, the temperature of the liquid, and other circumstances.

5. Affinity measured by Combining Proportions.

When Kirwan was engaged in his inquiries on the composition of salts, he remarked that each salt possessed a different percentage amount of acid and base, and he supposed that these might serve as a means of estimating the force of affinity. Tables were drawn up by Kirwan as follows :—

Table No. 1.

100 Grains.	Potash.	Soda.	Lime.	Ammonia.	Magnesia.	Alumina.
Sulphuric acid ..	215	165	110	90	80	75
Nitric acid	215	165	96	87	75	65
Muriatic acid ..	215	158	89	79	71	55

Table No. 2.

100 Grains.	Sulphuric acid.	Nitric acid.	Muriatic acid.
Potash	46·5	46·5	46·5
Soda	60·9	60·9	63·4
Lime	91·0	104·1	112·0
Ammonia..	111·1	115·0	126·5
Magnesia..	125·0	133·3	141·0
Alumina	133·3	153·6	181·8

Kirwan thus arrived at two general laws :—

(1.) *That the quantity of any base required to saturate a given quantity of any acid, was* DIRECTLY *as the affinities.*—Thus, potash had more affinity for sulphuric acid than soda, soda than lime, lime than ammonia, and so on.

(2.) *The quantity of any acid required to saturate any given quantity of a base, was* INVERSELY *as the affinities.*—Thus, sulphuric acid had more affinity for potash than it had for soda, nitric acid less affinity than sulphuric acid for lime, hydrochloric acid less than nitric acid, and so on. Bergman, arguing on the same facts, expressed the law of affinity differently : "*The force of affinity, whether of acid or base, is in the ratio of the quantities required to saturate.*" But it was manifest that this was not so, for the first table would show lime, for example, to have more affinity for sulphuric acid than for nitric acid, whilst the second table would indicate exactly the reverse.

Berthollet again, expressed what he deemed the law of affinity from the same facts as follows : "*The force of affinity is* INVERSELY *as the quantities required to saturate.*"

Again, as Sir H. Davy showed, Berthollet's law involved a contradiction, inasmuch as the action between the constituents of a compound must be mutual. "Sulphuric acid," writes Sir H. Davy, "has as much attraction for baryta as baryta for sulphuric acid. Now baryta is the alkaline earth of which the largest amount is required to saturate sulphuric acid, therefore on Berthollet's views, it has *the weakest affinity* for that acid. But less sulphuric acid saturates baryta than any other earthy or alkaline body, therefore, according to Berthollet, sulphuric acid has *a stronger affinity* for baryta than for any other substance, which is contradictory."

Again, experiment proves Berthollet's law fallacious. From his tables, such as the following, it would seem that ammonia had a greater affinity than baryta for sulphuric acid, and carbonic acid a greater affinity than sulphuric acid for baryta, which we know not to be the case :—

40 parts of Sulphuric acid require for neutralisation	77 parts of Baryta require for neutralisation
292 Morphia.	165 Iodic acid.
162 Quinine.	118 Bromic acid.
77 Baryta.	76 Chloric acid.
52 Strontia.	64 Nitric acid.
48 Potash.	49 Sulphuric acid.
32 Soda.	37 Muriatic acid.
28 Lime.	36 Oxalic acid.
20 Magnesia.	22 Carbonic acid.
17 Ammonia.	

Berthollet, however, was fully aware of the contradictory results, but explained them by the modifying effects of cohesion and elasticity.

It is certain, however, that combining proportions and power of saturation, are in no respect measures of relative affinity.

6. Affinity Measured by the Electrical Condition.

Becquerel was one of the first to point out that if a current of electricity of known activity be passed through a mixed solution of the metals, it decomposed them in a given order.

The subject of electrolysis, from the time that Faraday first commenced his researches, has grown in importance. We have already directed attention to certain details of the subject (p. 18).

CHAPTER II.

Nomenclature—Chemical Symbols and Formulæ—Combining Proportions—Atoms—Molecules—Atomic and Molecular Combination—Compound Radicals—Volume—Standard Pressure and Temperature—Relative Weight—The Crith—Relation between Atomic Weights and Specific Gravity — Relation between Atomic Weights and Specific Heats—Atomicity and Quantivalence—Chemical Formulæ—Substitution—Isomerism—Isomorphism—Allotropism—The Metric System.

Elements and Compounds.—By *an element* or *simple* body we understand a substance which cannot, so far as experiment has gone, be decomposed, and from which nothing can be taken but the substance itself. Iron is an element, because you can extract nothing from iron but iron. The elements are divided into two arbitrary classes—metals and non-metals.

By a *compound* body we understand one formed by the union of two or more elementary bodies. Common salt is a compound body. It may be formed by combining sodium and chlorine. From common salt we can obtain sodium and chlorine. The first is the *synthetical* proof, and the second the *analytical* proof, of its compound nature. The analytical experiment proves that common salt contains sodium and chlorine, whilst the synthetical experiment proves that it contains sodium and chlorine only.

Names of Bodies.—The ancient names given to bodies were mostly fanciful. They were derived either (α) *from their resemblance to certain things* (*e.g.*, oil of vitriol, sugar of lead, butter of antimony, liver of sulphur, etc.); or (β) *from some remarkable property of the body*; (*e.g.*, caustic alkali, corrosive sublimate, vital air, sal polychrest, phosphorus, antimony, etc.); or (γ) *from the name of a person or heathen divinity* (*e.g.*, Glauber's salts, Tantalum, Niobium, etc.); or (δ) *from the name of a place* (*e.g.*, Epsom salts, Cheltenham salts, Columbium, etc.); or (ε) *from the name of a planetary body* (*e.g.*, Tellurium, Uranium, etc.)

A reformation in nomenclature was suggested, in 1781, by Guyton Morveau, who proposed that the name should indicate somewhat the properties and composition of the body. In 1787, he obtained for this purpose the assistance of the French Academy of Sciences, and Lavoisier, Berthollet, and Fourcroy were appointed to join him in the work. To a large extent their efforts were successful.

Many of the names now employed express some special characteristic of the body. Thus chlorine (χλωρὸς, green) refers to the color of the substance; bromine (βρῶμος, stench) to its odor, etc. Most of the metals, although many of the common names are retained, are distinguished by the termination *um*. The haloid group terminate in *ine;* others terminate in *on*, as carbon and boron ; and others again in *gen* (γεννάω), as hydrogen (water-begetter), oxygen (acid-begetter), nitrogen (nitro-begetter), etc.

In the case of compounds, the name is made to express *the components* of the body, and, as far as possible, *its constitution*. Thus, the name " sodic chloride " expresses a compound of sodium and chlorine. The term "*anhydride*" signifies a binary compound containing oxygen (an oxide), which, when combined with water, forms an acid ; in other words, the residue obtained by abstracting all the displaceable hydrogen from one or two molecules of an oxygen acid.

For example—

$$\begin{array}{ccccc} SO_3 & + & H_2O & = & H_2SO_4. \\ \text{Sulphuric anhydride} & + & \text{Water} & = & \text{Sulphuric acid.} \end{array}$$

An inorganic pyro-acid, which is a partial anhydride, results from the elimination of water from two molecules of a polybasic acid. For example—

Phosphoric acid ($2H_3PO_4 - H_2O$) forms pyrophosphoric acid ($H_4P_2O_7$)
Sulphuric acid ($2H_2SO_4 - H_2O$) forms pyrosulphuric acid ($H_2S_2O_7$)

A pyro-acid, in organic chemistry, merely indicates a compound resulting from the application of heat to the original acid.

We may here consider the meaning of the various terminations and prefixes used in chemical nomenclature.

I. TERMINATIONS.

(1.) "*ide*" is applied to the negative constituent of a binary compound (that is, a compound formed by the union of two elementary bodies), the positive constituent frequently being made to terminate in "*ic*." For example—

Potassium + iodine form potassic (or potassium) iod*ide*.
Lead + oxygen „ plumbic (or lead) ox*ide*.

[NOTE.—Sir H. Davy suggested that the terminations in these cases should indicate property, "*ide*" being employed for acid, and "*uret*" for alkaline compounds.]

(2.) "*ic*" and "*ous*."—Two bodies may combine in different proportions. Thus, tin and chlorine combine to form $SnCl_2$ and $SnCl_4$. The termination *ic* is given to the *positive* constituent of the compound (Sn) containing the *largest* proportion of the *negative* constituent (Cl), and the termination *ous* to the *positive* constituent, containing the *smallest* proportion of the *negative* constituent. For example—

1 atom of tin + 2 chlorine = stann*ous* chloride ($SnCl_2$).
1 atom of tin + 4 chlorine = stann*ic* chloride ($SnCl_4$).

(Similarly FeO = ferr*ous* oxide, Fe_2O_3 = ferr*ic* oxide; Hg_2O = mercur*ous* oxide, HgO = mercur*ic* oxide; etc.)

These terminations "*ic*" and "*ous*," moreover, are employed to distinguish acids that are composed of the same elements, but in different proportions. Thus, sulphur forms two acids by its combination with oxygen. The acid which contains the most oxygen is called sulphur*ic* acid, whilst that containing the least oxygen is called sulphur*ous* acid.

Sulphur*ous* acid	Contain less oxygen than	Sulphur*ic* acid.
Phosphor*ous* acid		Phosphor*ic* acid.
Nitr*ous* acid		Nitr*ic* acid.

(3.) "*ite*" and "*ate*."—The termination "*ite*" implies that the salt is a compound of a base with an acid terminating in "*ous*," and the termination "*ate*" that the salt is a compound of a base with an acid terminating in "*ic*." For example—

Sodic sulph*ite* is a sodium salt of sulphur*ous* acid.
Sodic sulph*ate* „ sulphur*ic* acid.

(4.) "*a*" and "*ia*."—The termination "*a*" is usually given to inorganic alkalies, such as soda, and "*ia*" to organic alkalies, such as strychnia. The rule is not absolute.

(5.) "*ine*" or "*in*" are used to denote a neutral active principle, such as caffeine, piperin, etc.

(6.) "*yl*" or "*yle*" is adopted in the case of many of the compound radicals, such as methyl, propyl, etc.

II. Prefixes.

(1.) *Bin, Ter,* etc. (Latin); or *Mon,* or *Mono, Deut.*, etc. (Greek); or *Di, Tri, Tetra,* etc., denote various proportions of constituents, and the position of various compounds in a series. For example—

Carbon monoxide (or carbonic oxide) signifies $C + O$.
Carbon dioxide (or carbonic anhydride) „ $C + O_2$.

There is no rule as to the use of the Latin or the Greek forms.

(2.) "*Per*" denotes the highest compound in a series. For example, a *peroxide* signifies that oxide which contains the largest quantity of oxygen in a series of oxides.

(3.) "*Sesqui*" denotes a compound where the relationship of the elementary atoms is as 2 to 3; for example, sesquioxide of iron (really ferric oxide) has the formula Fe_2O_3.

(4.) "*Proto*" (πρῶτος, first) denotes the first of a series of compounds; for example, the protoxide of iron FeO (also called ferr*ous* oxide) contains the smallest quantity of oxygen of any iron and oxygen compound.

(5.) "*Hypo*" (ὑπὸ, under) denotes the position of a compound. Thus, the acid containing *less* oxgen than *phosphorous acid*, might be called *hypophosphorous* acid.

(6.) "*Hyper*" (ὑπὲρ, over) is occasionally used to express the converse of the prefix "hypo."

(7.) "*Para*" signifies equal; for example, *para*cyanogen implies a body chemically equal to cyanogen.

(8.) "*Meta*" signifies "near to." Thus, *meta*phosphoric acid only differs from orthophosphoric acid by 1 molecule of water.

(9.) "*Sub*" implies that the compound contains less of a constituent than is indicated by the rest of the word.

(10.) "*Sulph*" or "*Sulpho*," "*Hydr*" or "*Hydro*."—The composition of acids formed by the combination of sulphur or hydrogen (*without oxygen*) with other elements is expressed by the foregoing prefixes, the terminals "*ous*" and "*ic*" being also employed in the case of the sulphur compounds to indicate the proportions of sulphur relatively present. In the case of hydrogen, such terminations are not needed, inasmuch as only one acid is formed by the union of an element with hydrogen.

Chemical Symbols and Formulæ.

The alchymists adopted signs to represent bodies. Thus ⊙ (sol) represented gold, and ☽ (luna) silver, etc. Chemists now-a-days denote the various elementary bodies by symbols, using either the first letter of the Latin name, or, where several elements have the same initial letter, the first letter subjoined with a smaller one. Thus O = oxygen; C = carbon; Ca = calcium; Cl = chlorine, etc.

Further, this symbol represents one equivalent or combining weight of the element. Thus, the symbol O represents *a similar bulk* of oxygen that the symbol H represents of hydrogen, but *a weight* 16 times as great.

A compound is represented by the symbols of the several components placed one after the other. Thus, HCl represents a compound, formed of one atom of hydrogen and one of chlorine, or by 1 part by weight of hydrogen and 35·5 parts by weight of chlorine.

If we desire to express more than one atomic proportion, we place a little figure above or below the symbol. Thus H_2O or H^2O imply that with every atom or 1 atomic part by weight of oxygen, there is conjoined 2 atoms or 2 atomic parts by weight of hydrogen.

If the figure be placed before the whole formula, it implies that all the elements composing the group, *i.e.*, either as far as a comma, or some other sign following, or else included in brackets immediately succeeding the number, are to be multiplied by the said number. Thus in the equation* $Ca_3P_2O_8 + 2(H_2SO_4) = 2(CaSO_4) + H_4CaP_2O_8$, the 2 before the H_2SO_4 and the 2 before the $CaSO_4$ imply that the whole numbers are to be multiplied by 2; but there being a + after the $CaSO_4$, it follows that the $H_4CaP_2O_8$ is *not* to be multiplied by the 2 preceding the $CaSO_4$.

It is not, however, necessary to employ brackets unless a comma be introduced into the formula; thus, in the equation—

$$Ca_3P_2O_8 + 2H_2SO_4 = 2CaSO_4 + H_4CaP_2O_8$$

the multiplication of the H_2SO_4 and of the $CaSO_4$ respectively by 2 is as much indicated as though the formulæ had been placed within brackets. Thus, the formula $3Cu,2NO_3$ implies that the Cu only is to be multiplied by 3, and not the $2NO_3$; whilst if the formula following the number be placed in brackets, thus $3(Cu,2NO_3)$, it then implies that the whole number is to multiplied by 3. Thus—

$$\begin{array}{lll} 3Cu,2NO_3 & \text{would be equivalent to} & Cu_3N_2O_6\text{; but} \\ \left.\begin{array}{l} 3Cu2NO_3 \text{ or} \\ 3(Cu,2NO_3) \end{array}\right\} & \text{,,} \qquad \text{,,} & Cu_3N_6O_{18}. \end{array}$$

Combining Proportions—Atomic Theory.

In 1774, Wenzel, a German chemist, published a work on "The General Theory of Affinities." This in reality, contained the germ of the atomic theory. The great fact noted by Wenzel was, that when two neutral salts, such as sodic sulphate and plumbic acetate, were mixed together, although an exchange of acids took place, the resulting products were neutral, proving that the acid of the one salt was sufficient to neutralize the base of the other salt.

In 1792, Richter, a Prussian chemist, wrote a work on "Stochiometry, or the Mathematics of Chemical Elements" (στοιχεῖον, an element, μετρέω, I measure). This was mainly directed to illustrating the relative quantities of acid and base necessary for saturation. He further constructed numerous tables, such as the following, as the result of his inquiries†:—

---

[*] A chemical "*equation*" signifies the expression of chemical reactions by chemical formulæ.

It will be remarked that in chemical, as in algebraical equations, the sign + signifies addition (or admixture); the sign — subtraction; and the sign = equals (or yields, or is converted into).

[†] These tables are taken from Thompson, and represent the mutual combining proportions of acid and base.

1. *Acids.*

Fluoric	427
Carbonic	577
Sebacic	706
Muriatic	712
Oxalic	755
Phosphoric	979
Formic	988
Sulphuric	1000
Succinic	1209
Nitric	1405
Acetic	1480
Citric	1683
Tartaric	1694

2. *Bases.*

Alumina	525
Magnesia	615
Ammonia	672
Lime	793
Soda	859
Strontia	1329
Potash	1605
Barytes	2222

In 1800, whilst Dalton was analysing some compounds of hydrogen and carbon, he remarked that the several quantities advanced in multiple proportions. The same, moreover, he found to be true with other compounds, such as those of carbon and oxygen, sulphur and oxygen, etc. It therefore occurred to him “ *that matter was composed of particles of definite weights, and that it combined in those weights.*

This constituted Dalton's “ Atomic Theory,” the fundamental propositions of which are—

(1.) That matter is composed of indivisible and indestructible particles called *atoms.*

(2.) That the atoms in a mass do not touch, but are surrounded by an atmosphere of heat.

(3.) That the atoms are endowed with attractive and repulsive forces.

(4.) That they have specific weights.

Atoms (*α*, *not*, and *τέμνω*, *I cut*).—Here we refer entirely to the atoms of elementary bodies and not to “ *compound radicals*,” which have been called “ *compound atoms*.”

(1.) Every element consists of ultimate particles called “ *atoms*.” The chemical symbol of any element represents this atom. Thus, O represents the atom or smallest indivisible particle of oxygen.

(2.) We have no actual knowledge either of *the shape, the absolute weight*, or *the absolute volume* of these atoms.

(3.) The atoms of any given substance are believed to be of identical weight, under any and every condition. In other words, one atom of oxygen weighs the same as every other atom of oxygen.

(4.) Nevertheless the atom of one body does not weigh the same as the atom of every other body. An atom of oxygen weighs 16 times as much as, and an atom of carbon 12 times as much as, an atom of hydrogen. These *comparison weights* of the atoms (hydrogen, as the lightest body known, being regarded as 1) are called *atomic weights.* Atomic weights, therefore, are *relative weights*, but not *absolute weights.* For example, when we say that mercury has an atomic weight of 200, we mean that the atom of mercury would weigh 200 times as much as the atom of hydrogen, but inasmuch as we cannot determine the absolute weight of the hydrogen atom, the number 200 does not express the absolute weight of the mercury atom.

Accurately, we may define the *atomic weight* of an element, as "*that weight which would occupy in the state of gas the same volume as the unit weight of hydrogen under like temperature and pressure.*"

If, however, we cannot obtain the element in a state of gas (as, *e.g.*, in the case of carbon), the atomic weight is then deduced from such other considerations as the specific heat of the body, etc.

The atomic weights have been determined by analyses of great delicacy—simple compounds being mainly selected for the purpose—varying the process of analysis, and varying the compound analysed, to prevent error. Further, in fixing atomic weights assistance is derived from its specific heat, the density of its vapour, the isomorphism of compounds, etc.

By the term "*combining proportion*" Sir H. Davy implied the smallest proportion *by weight* (hydrogen being regarded as unity) with which bodies combine with each other.

Molecule (*Molecula, a little mass*).—These may be compound or elementary:—

(*a.*) *Compound Molecules.* A compound body is made up of two or more elementary atoms. A molecule of any given compound is "*the smallest possible cluster of elementary atoms capable of existing as the compound, and of possessing independent chemical action.*" Thus a molecule of water (H_2O) consists of 2 hydrogen atoms and 1 oxygen atom. The water molecule therefore consists of 3 atoms, inasmuch as nothing less than an aggregate of 3 atoms can form water. Or again, a molecule of ammonia (NH_3) consists of 4 atoms, viz., 3 of hydrogen and 1 of nitrogen. It could not be ammonia if there were less than 4 atoms present in the molecule. *A compound molecule, therefore, may be a cluster of any number of atoms from two upwards.*

The atomic weight of a molecule is the sum of the weights of the several atoms of which it is composed. Thus 18 is the atomic weight of a molecule of water ($H_2O = 2 + 16$). The molecular weight of a hydrogen salt is always that weight which contains as many hydrogen atoms as can be replaced by potassium, silver, etc. Thus $H_2C_2O_4$ (that is, twice its empirical formula) is the formula for a molecule of oxalic acid, and 90 its molecular weight, because whilst we are able to replace both the atoms of hydrogen by potassium, forming the *neutral potassic oxalate*, $K_2C_2O_4$, we may also replace one hydrogen atom only by potassium, thereby forming the acid salt, *hydric potassic oxalate*, HKC_2O_4. Thus we regard oxalic acid as a dibasic acid.

Conversely, we represent 63 as the molecular weight of HNO_3, and not 126 (viz., $H_2N_2O_6$), because, whilst we have the salt KNO_3, we know of no such salt as HKN_2O_6. Nitric acid, therefore, is a monobasic acid.

The symbol of a *compound* body represents a molecule of that body.

(*b*.) *Elementary molecules.*—There are strong reasons for believing that our knowledge of the reaction of elements pertains rather to their *molecular* than to their *atomic* condition, and that in all decompositions and combinations the molecule of the element is concerned, although only one of the atoms of the molecule may be at work in effecting the change. Thus a free element, such as hydrogen, never appears to work singly, but in clusters. In a bottle of hydrogen, therefore, we should regard the gas, not as made up of atoms of $\boxed{\text{H}} = 1$, but of atom-clusters of $\boxed{\text{H} \mid \text{H}} = 2$. The convenience of this diatomic symbolization, as it is called, will appear further, when we note that, with very few exceptions, compound bodies in their vaporous condition, occupy two volumes. This leads us to define—

An atom of an elementary body as the smallest proportional weight capable of existing in chemical combination; and

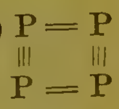
A molecule of an elementary body as the smallest proportional weight capable of existing in a free or uncombined state.

By the phrase *molecular weight*, then, we imply "the weight of *two* volumes of any substance, elementary or compound, compared with the weight of two volumes of hydrogen." Thus—

$H_2 = 2$: Therefore the molecular weight of $O_2 = 32$, of $Cl_2 = 71$, of $HCl = 36{\cdot}5$.

Dr. Frankland expresses this fact by stating that no element can exist with any of its bonds unconnected, and that, therefore, the molecules of all elements having an uneven number of bonds are generally diatomic, but always polyatomic. Thus—

Hydrogen (H'_2) H—H; *Nitrogen* (N^{v}_2) $N \mathrel{\overset{=}{\equiv}} N$; *Phosphorus* (P^{v}_4)

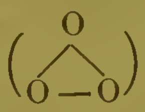


$$\begin{array}{ccc} P & = & P \\ ||| & & ||| \\ P & = & P \end{array}$$

In some cases (viz., mercury, zinc, and cadmium) we find an element capable of existing as a monatomic molecule, its own bonds satisfying one another. In such case, however, the atomicity must be even (artiad). Thus—

Mercury (Hg'') $\lfloor\!-\text{Hg}-\!\rfloor$; *Zinc* (Zn'') $\lfloor\!-\text{Zn}-\!\rfloor$; *Cadmium* (Cd'') $\lfloor\!-\text{Cd}-\!\rfloor$.

On the other hand, such an element may also be polyatomic. In ozone, an allotropic form of oxygen, for example, the molecule is triatomic. Thus, whilst O_2 $(O = O)$ represents the ordinary diatomic molecule of oxygen, O_3



represents the triatomic molecule of ozone.

COMBINATION BY WEIGHT.

The laws of chemical combination as taught by Dalton are as follows :—

I. *That every definite chemical compound has a fixed and invariable composition ; that is, a given compound always consists of the same elements united in the same proportions.*

Thus, hydrochloric acid (HCl) consists of 1 atom of hydrogen (H) combined with 1 atom of chlorine (Cl). The weight of the hydrogen atom being 1, and the chlorine atom 35·5, it follows that in every 36·5 grains, or pounds, or tons of hydrochloric acid, there is 1 grain, or pound, or ton of hydrogen, and 35·5 grains, or pounds, or tons of chlorine. Hydrochloric acid can be formed in no other proportion than 1 part of hydrogen to 35·5 parts of chlorine.

II. *If one substance combines with another in more than one proportion, the several proportions are always some multiple or sub-multiple of the lowest of these proportions.*

This is illustrated, for example, in the oxides of nitrogen:—

			Atomic weight of Nitrogen.		Atomic weight of Oxygen.
Nitrous oxide..........	N_2O	....	$14 \times 2 = 28$	to	16.
Nitric oxide	N_2O_2	....	28	to	$16 \times 2 = 32$.
Nitrous anhydride......	N_2O_3	....	28	to	$16 \times 3 = 48$.
Nitric peroxide	N_2O_4	....	28	to	$16 \times 4 = 64$.
Nitric anhydride	N_2O_5	....	28	to	$16 \times 5 = 80$.

It will be seen how the various quantities of oxygen increase by definite multiples of 16. It often happens, however, that a series may be deficient, or that the proportions are less simple than in the illustration given.

III. *If the weights in which a series of bodies* (B, C, D, E, etc.) *combine with another body* (A) *be determined, these weights or some multiple or sub-multiple thereof, are also the weights with which* B, C, D, *and* E *combine amongst themselves :—*

Example: 16 of oxygen will combine with 65 of zinc, and
$16 \times 2 = 32$ of oxygen „ 32 of sulphur;
Therefore 65 of zinc „ 32 of sulphur.

IV. *In a compound body, the combining weight of the compound is the total combining weight of the components.*

For example, the combining weight of sulphur is 32, and of oxygen 16. The combining weight of sulphuric anhydride (SO_3), which is composed of 1 of sulphur and 3 of oxygen, is, therefore, 80.

These facts give accuracy to all chemical reactions. In the laboratory no materials are mixed at random ; bodies combine in exact proportions, and form products of definite weights. It follows that, "*As the total molecular weight of the substance given is to the total molecular weight of the substance required, so is the given weight to the required weight.*"

That is, if we desire to obtain 500 grammes of carbonic anhydride from sodic carbonate, knowing that every 106 parts of sodic carbonate contain 44 parts of carbonic anhydride, the exact quantity of sodic carbonate necessary to produce the 500 grammes (x) may be estimated by the equation—

$$\frac{106 \times 500}{44} = x.$$

Atomic and Molecular Combination.—H represents an atom of hydrogen. H_2 represents a molecule of hydrogen, *i.e.*, the smallest portion of hydrogen capable of existing in the free state. Cl similarly represents an atom, and Cl_2 a molecule of chlorine. To express the combination of these bodies in *atomic formula* we write it thus—

$$Cl + H = HCl,$$

whilst to express their combination in *molecular formula* we write it thus—

$$Cl_2 + H_2 = 2HCl,$$

this latter implying the bringing together and the mutual interchange of two molecules, whereby two molecules of a new body are formed. As regards the relative weights of the constituents and of the resultant, it does not matter which way the equation is written.

Two molecules occasionally, though rarely, unite to form one molecule, from the latent atomicity of an element becoming active. Thus in phosgene gas—

$$''C''O + Cl_2 = C^{iv}OCl_2 \text{ (phosgene gas)},$$

the *latent* atomicity of the carbon in the CO becomes *active* in the $COCl_2$, thereby making the active atomicity of the carbon in the latter compound double what it was in the former.

There is what Frankland calls a *molecular union* or *combination*, where no change results in the active atomicities of any of the molecules; such, for example, is the combination of salts with their water of crystallisation.

Compound Radicals.—A compound radical (in contradistinction to an element, which may be called "a simple radical") is "*a compound group of two or more atoms, which behaves in all respects as though it were an element.*"

Such compound groupings were supposed by Liebig to be peculiar to bodies of organic origin, but their existence is now recognised amongst inorganic substances.

Theoretically, the number of compound radicals must be endless. Practically, however, chemists only term those groupings compound radicals, that can be shown to enter into the composition of a large number of compounds.

Respecting these compound radicals we would note that—

(1.) Every compound radical must contain a polyad element—that is, an element requiring two or more hydrogen atoms, or their equivalent, to saturate it.

(2.) Compound radicals, like the elements, are of different atomicities, the atomicity depending on the number of hydrogen or other monad atoms required to satisfy them. Thus—

If you remove H from the fully saturated NH_3 (ammonia) an unsaturated "residue" or "compound radical," amidogen (NH_2) remains, of *monad* atomicity. Thus, amidogen will combine with the monad element potassium, to form potass-amine (NH_2K).

If H_2 be removed from NH_3, an unsaturated radical remains (imidogen (NH)), of *dyad* atomicity. Thus, imidogen will combine with two of the monad compound radical methyl (CH_3) to form dimethyl-amine $NH(CH_3)_2$.

(3.) The molecule of a monad, triad, or pentad compound radical, like the atom of a monad, triad, or pentad element, cannot exist in a free state, but when isolated combines with itself. Thus just as H_2 represents a molecule of hydrogen, so $(HO)_2$ represents a molecule of the monad compound radical hydroxyl.

In *organic* chemistry compound radicals are endless. The first recognised, well-marked compound organic radical was cyanogen (CN or Cy). Like chlorine, which combines with hydrogen to form hydrochloric acid (HCl), it combines with hydrogen to form hydrocyanic acid (HCy), the combination of two volumes being effected in both cases without condensation.

Volume (*volvo,* I roll).—"A volume" in chemical language implies the space occupied by a known weight of a gas at a given temperature and pressure, compared with the space occupied by known weights of other gases at similar temperature and pressure.

As in compound bodies the elementary atoms combine in fixed weights (proved by Dalton), so in gaseous compounds, the constituents combine in fixed volumes (proved by Gay Lussac, 1809).

The symbols H, O, Cl represent atoms of hydrogen, oxygen, and chlorine, having the relative weights 1, 16, and 35·5 respectively. If we take 1 gramme of hydrogen we should find that at a certain temperature and pressure the volume of the gas would measure 11·2 litres. In order to obtain a volume of oxygen measuring 11·2 litres, or a volume of chlorine measuring 11·2 litres at a similar temperature and pressure, we should require in the former case 16 grammes, and in the latter case 35·5 grammes. These weights are, it will be noticed, the atomic weights of oxygen and chlorine. *Hence, the symbols* H, O, *and* Cl *represent different weights of the gases, but similar bulks.*

Again, imagine this □ to represent a separate volume of hydrogen, or oxygen, or chlorine. If this volume of hydrogen weighed 1 grain, a similar volume of oxygen would weigh 16 grains, and a similar volume of chlorine would weigh 35·5 grains. *Hence the symbols* H, O, Cl *represent similar bulks of the several gases, but different weights.*

These facts were first noted in 1811 by Amãdeo Avogadro, and were discussed in detail in 1814 by Ampère. Avogadro noted that the effect of changes of temperature and pressure on all gases was alike, and reasoning on this constancy of results, he concluded "*that equal volumes of all substances (elementary or compound) in a gaseous state contain under like physical conditions (i.e., at the same temperature and pressure) the same number of molecules*" ("Journal de Physique," July, 1811). But, inasmuch as equal volumes had different weights, it followed that the molecules of different gases must also have different weights, such different weights being proportional to the weights of equal volumes at the same temperature and pressure (*i.e.*, their vapour densities).

An illustration will make these facts clear:—

(*a.*) The *volume combination* of hydrogen and chlorine to form hydrochloric acid may be thus expressed,

$$\boxed{\mathrm{H}} + \boxed{\mathrm{Cl}} = \boxed{\mathrm{H} \vdots \mathrm{Cl}};$$

which implies that a given volume of hydrogen combines with a similar volume of chlorine to form two volumes of hydrochloric acid.

(*β.*) The *weight-combination* of hydrogen and chlorine is expressed thus—

$$\mathrm{H} + \mathrm{Cl} = \mathrm{HCl};$$

which implies that 1 part by weight of hydrogen combines with 35·5 parts by weight of chlorine to form 36·5 parts by weight of hydrochloric acid.

(*γ.*) If therefore the hydrogen volume has a weight of 1, the chlorine volume must have a weight 35·5 times as great. If, however, both volumes contain the same number of molecules, it follows that the weight of the chlorine molecule must be 35·5 times that of the hydrogen molecule.

(*δ.*) It is evident that the volumes of any two gases forming a compound, are to one another as the atoms of the elements forming the compound. Thus—

$\mathrm{H} + \mathrm{Cl} = \mathrm{HCl}$; implies that $\left\{\begin{array}{l}\text{1 atom of H combines with 1 atom of Cl,}\\ \text{or}\\ \text{1 vol. of H combines with 1 vol. of Cl.}\end{array}\right.$

$\mathrm{H_2} + \mathrm{O} = \mathrm{H_2O}$; implies that $\left\{\begin{array}{l}\text{2 atoms of H combine with 1 atom of O,}\\ \text{or}\\ \text{2 vols. of H combine with 1 vol. of O.}\end{array}\right.$

(*ε.*) To this law there are certain exceptions :—

(1.) In the case of *Phosphorus* and *Arsenic*, the *number of volumes* *must be halved.* In other words the molecules of these bodies are tetratomic. Thus :—

In PH_3 $\begin{cases} \text{3 vols. of H combine with } \frac{1}{2} \text{ vol. of P vapour ; or} \\ \text{6 vols. of H combine with 1 vol. of P vapour.} \end{cases}$

In AsH_3 $\begin{cases} \text{3 vols. of H combine with } \frac{1}{2} \text{ vol. of As vapour ; or} \\ \text{6 vols. of H combine with 1 vol. of As vapour.} \end{cases}$

(2.) In the case of *mercury, zinc, and cadmium,* the number of volumes must be doubled (p. 34). In other words, the molecules of these bodies are monatomic, and consequently their molecular and atomic weights are identical. Thus :—

In $HgCl_2$ 2 vols. of mercury vapour combine with 2 vols. of chlorine.

Hence, the general facts may be stated as follows :—" The combining volumes of all elementary gases are equal, excepting phosphorus and arsenic, which are *one-half,* and zinc, mercury, and cadmium, which are *double* those of the other elements in the gaseous state."

To this may be added that the sulphur molecule at 975·2° F. (524° C.) is hexatomic, but that this at 1580° F. (860° C.) breaks up into three diatomic molecules.

STANDARD PRESSURE AND TEMPERATURE.

In connection with our study of volume-combination, it is important to understand the method of correcting gases to standard temperature and pressure, when the volume is estimated at irregular temperatures and pressures.

By standard pressure is meant when the barometer stands at 760 millimètres (really 29·92 inches), and by *standard temperature,* 0° Centigrade.

(1.)—**Standard Pressure.**—This implies "*the pressure of a column of mercury of* 760 *mm., at* 0° *C.*"

By the term "1 pressure" or "1 atmosphere" is implied the weight of a 760 mm. column of mercury, this being the quantity which the air (on an average) is capable of supporting. Such a column is found to press with a weight of 15 lbs. on the square inch. A pressure of 15 lbs. on the square inch, therefore, constitutes what is called "1 pressure" or "1 atmosphere ;" a pressure of 30 lbs. on the square inch constituting "2 pressures" or "2 atmospheres," etc.

The relationship of the volume of a gas to pressure, known as the Law of Boyle and Marriotte (1662) is as follows :—"*Temperature being constant, the volume of a gas varies inversely as the pressure* ;" in other words, the pressure of a gas is proportional to its density ; the smaller the pressure the greater the volume, the greater the pressure the smaller the volume.

A given quantity of any gas at 1 pressure = 1 volume.
" " 2 pressures = $\frac{1}{2}$ volume.
" " 4 pressures = $\frac{1}{4}$ volume.
" " $\frac{1}{2}$ pressure = 2 volumes.
" " $\frac{1}{4}$ pressure = 4 volumes.

Or the facts may be stated thus :—

1 litre of gas at (30 in. B.P.) 760 mm. would occupy 2 litres at (15 in. B.P.) 380 mm., and 0·5 litre at (60 in. B.P.) 1,520 mm. ; or 100 cubic inches at 1 pressure would become 50 cubic inches under a pressure of 2 atmospheres, and 200 cubic inches under a pressure of half an atmosphere.

To correct a gas, therefore, from an irregular pressure to the standard pressure, the simple rule is,—

As the required pressure (*i.e.*, 30 in. or 760 mm.) *is to the given pressure, so is the given bulk to the required bulk.*

Examples—

(α.) If a gas occupies 250 cubic in. at 29·2 in. B.P., what bulk will it occupy at standard pressure?

30 : 29·2 : : 250 : *x*. *Ans.* 243·3 c. i.

(β.) If at 754 mm. a gas measures 1·25 litres, what will it measure at standard temperature?

760 : 754 : : 1·25 : *x*. *Ans.* 1·240 litre.

(γ.) What bulk will a gas occupy at 29 in. B.P. which measures 0·6 litre at 30 in.

29 : 30 : : 0·6 : *x*. *Ans.* 0·62 litre.

It should be noted that Boyle's law is only approximately true, deviations being observed under high pressures.

(2.)—Standard Temperature.—The law of Charles states that "*Pressure being constant, the volume of a gas varies directly as the absolute temperature*," in other words, a given volume expands equally for equal increments of heat.

The standard temperature is regarded as 0° C.

The law of Charles therefore declares, that all gases, unlike solids and liquids, expand by heat and contract by cold *regularly* for every increase or decrease of temperature, providing the pressure remains constant. *What, then, is this regular increase?* Experiment proves that it is an increase of the $\frac{1}{273}$ part of the volume (or 0·003665) for every 1° C. This fraction is termed "the co-efficient of expansion of gases" [= the $\frac{1}{490}$ part (or 0·00204) for every 1° Fahr.]. Hence—

273 vols. at 0° C. become 274 vols. at 1° C.
273 " " 373 " 100° C.
273 " " 546 " 273° C.

If, therefore, a gas measures a litre at 273° C., it will only measure half a litre at 0° C., pressure being constant.

To correct for temperature, the rule is,—

"*As* 273 + *the given temperature* (*in Centigrade degrees*) *is to* 273 + *the required temperature, so is the given bulk to the required bulk.*"

Examples—

(*a.*) A gas measures 1 litre at 273·0° C., what will it measure at 0° C. (standard temperature)?

$273 + 273 \; : \; 273 + 0 \; :: \; 1 \; : \; x.$ *Ans.* $x = 0{\cdot}5$ litre.

(β.) A gas measures 25 cubic in. at 20° C., what will it measure at the standard temperature?

$273 + 20 \; : \; 273 + 0 \; :: \; 25 \; : \; x.$ *Ans.* $x = 23{\cdot}29$ c. i.

In stating, therefore, the volume of a gas, it must in all cases be corrected (1) *to standard pressure* (30 in. or 760 mm.), the bulk of the gas varying, according to the law of Boyle, "*inversely as the pressure;*" and (2) *to standard temperature* (0° C.), the bulk of the gas varying, according to the law of Charles, "*directly as the temperature.*"

MOLECULAR COMBINATION. COMBINATION BY VOLUME. DOCTRINE OF TYPES.

(1.) *A molecule of hydrogen* $\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}$ is represented thus $\boxed{\mathrm{H} \,\vdots\, \mathrm{H}}$ (*Hydrogen Type*).

One of the H atoms of the molecule, may be replaced by one or other of the haloid elements (Cl, Br, I, F), to form a hydracid; thus—

$$\boxed{\mathrm{H}} + \boxed{\mathrm{Cl}} = \boxed{\mathrm{H} \,\vdots\, \mathrm{Cl}} \text{ or } 1 + 35{\cdot}5 = 36{\cdot}5.$$

1 vol. + 1 vol. = 2 vols.

Such acid may be represented as the combination of 2 volumes of chlorine (1 molecule) with 2 volumes (1 molecule) of hydrogen, four volumes of hydrochloric acid gas resulting—

$$\boxed{\mathrm{H} \,\vdots\, \mathrm{H}} + \boxed{\mathrm{Cl} \,\vdots\, \mathrm{Cl}} = \boxed{\begin{array}{c:c} \mathrm{HCl} & \mathrm{HCl} \\ \hdashline \mathrm{HCl} & \mathrm{HCl} \end{array}}$$

Whenever 1 *volume of one gas combines with one volume of a second gas, no condensation results; that is, the bulk of the compound formed is the same as the bulk of the two gases, and the weight as the weight of the two gases from which it was produced.* The fact, therefore, is that—

1 *litre of chlorine* + 1 *litre of hydrogen* = 2 *litres of hydrochloric acid gas.*

Or, in other words, a given bulk of hydrochloric acid gas is one-half hydrogen and one-half chlorine. The same is also true of hydriodic acid, hydrobromic acid, &c., bodies formed on the hydrogen type.

(2.) $\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}$ represents *a molecule of water* (*Water Type*).

Whenever 2 *volumes of one gas combine with* 1 *volume of another gas, they suffer condensation to the extent of* $\frac{1}{3}$; *that is, the bulk of the compound* *formed is only ⅔ that of the orginal gases from which it was produced, nevertheless the weight of the two volumes so formed, is the total weight of the three volumes that formed them.* Thus—

$$\begin{array}{ccccc} \boxed{H \,\vdots\, H} & + & \boxed{O} & = & \boxed{H_2 \vdots O} \quad \text{or } 2 + 16 = 18. \\ \text{2 vols.} & + & \text{1 vol.} & = & \text{2 vols.} \end{array}$$

This again, constitutes a type of another group of compounds, such as H_2S, H_2Se, etc.

(3.) $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$ represents *a molecule of ammonia gas* (*Ammonia Type*).

Whenever 3 *volumes of one gas combine with* 1 *volume of another gas, they suffer condensation to the extent of* ½ ; *that is, the bulk of the compound formed is only one-half that of the original gases from which it was produced, nevertheless the weight of the two volumes so formed, is the total weight of the four volumes that formed them.* Thus—

$$\begin{array}{ccccc} \boxed{H \,\vdots\, H \,\vdots\, H} & + & \boxed{N} & = & \boxed{N \vdots H_3} \quad \text{or } 3 + 14 = 17. \\ \text{3 vols.} & + & \text{1 vol.} & = & \text{2 vols.} \end{array}$$

(4.) $\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C$ represents *a molecule of marsh gas* (*Marsh Gas Type*).

Whenever 4 *volumes of one gas combine with* 1 *volume of another gas, they suffer condensation to the extent of* ⅗ ; *that is, the five volumes, after combination, only measure two volumes, nevertheless the weight of the two volumes so formed, is the total weight of the five volumes that formed them.* Thus—

$$\begin{array}{ccccc} \boxed{H \mid H \mid H \mid H} & + & \boxed{C} & = & \boxed{C \vdots H_4} \quad \text{or } 4 + 12 = 16. \\ \text{4 vols.} & + & \text{1 vol.} & = & \text{2 vols.} \end{array}$$

It would thus appear that the molecules of compound bodies in the gaseous state, occupy twice the volume of an atom of hydrogen gas ; all compounds, no matter what the number of atoms or volumes may be of which they are composed, becoming condensed into 2 volumes.

Relative Weights of Compound and Elementary Gases.

By the *Specific Gravity* of a gas we imply its weight compared with *air*.

By the *relative weight* of a gas we imply its weight compared with *hydrogen*.

(*a.*) In the case of the *elementary gases*, it is manifest that their *atomic* weights must be also their *relative* weights. A given volume of oxygen weighs 16 times as much as a similar volume of hydrogen ;—16, therefore, is the relative weight of oxygen.

(β.) In the case of *compound gases* it must be remembered that after combination *two* volumes are formed. Hence the relative weight of any compound gas is the sum of the weights of the component elements divided by 2. For example, a volume of hydrogen (1) and a volume of chlorine (35·5) form *two* volumes of hydrochloric acid gas. Hence $\left(\frac{36\cdot5}{2}\right)$ 18·25 in the relative weight of hydrochloric acid gas ;—in other words, hydrochloric acid gas is 18·25 times heavier than hydrogen. Similarly water gas is $\left(\frac{18}{2}\right)$ 9 times heavier than hydrogen, and ammonia gas $\left(\frac{17}{2}\right)$ 8·5 times, and marsh gas $\left(\frac{16}{2}\right)$ 8 times heavier. These numbers, therefore, constitute the relative weights of these compound gases.

Unit of Volume.—The Crith.—Hydrogen, being the lightest known gas, is regarded not only as *the unit of weight*, but as *the unit of volume*. A litre of hydrogen weighs 0·0896 grm. (exactly 0·089578 grm.), this number being called a crith (κριθὴ, a barleycorn).

(α.) The weight of a litre of any *elementary* gas, is found by multiplying 0·0896 grm. (*i.e.*, the weight of a litre of hydrogen) by its atomic weight. Thus—

1 litre of oxygen weighs 0·0896 × 16 = 1·433 grm.
1 litre of nitrogen ,, 0·0896 × 14 = 1·254 grm.

100 cubic inches of hydrogen at 60° F. and 30 inches Bar. Pr. weigh 2·143 grains. The weight of 100 cubic inches of any elementary gas at similar temperature and pressure is found by multiplying this number by the atomic weight.

(β.) The weight of a litre of any *compound* gas is found by multiplying 0·0896 grm. by *half its molecular weight*, the molecular weight represents two volumes. [So also the weight of 100 cubic inches of any compound gas at 60° F. and 30° Bar. is found by multiplying 2·143 grains by half its molecular weight.] Thus—

1 litre of water gas (mol. wt. 18) weighs 0·0896 × 9=0·806 grm.
1 litre of carbonic anhyd. (mol. wt. 44) ,, 0·0896 × 22=1·917 grm.
1 litre of marsh gas (mol. wt. 16) ,, 0·0896 × 8=0·716 grm.

II. A gramme (15·432 grains) of hydrogen at 0° C. and at 760 mm. measures 11·2 litres. Therefore the atomic weights of the elementary gases, and half the molecular weights of the compound gases, represent in grammes the quantity necessary to occupy 11·2 litres.

(α.) 1 grm. of hydrogen measures 11·2 litres.
16 grms. of oxygen ,, 11·2 litres.
14 ,, of nitrogen ,, 11·2 litres.

(β.) 9 (*i.e.* 18 ÷ 2) grms. of water gas measure 11·2 litres.
22 (*i.e.* 44 ÷ 2) „ of carbonic anhydride measure 11·2 litres.
8 (*i.e.* 16 ÷ 2) „ of marsh gas measure 11·2 litres.

Relation between Atomic Weights and Specific Gravity. Atomic Volume.—So far as *solids and liquids* are concerned, no simple, if even any definite relationship has as yet been traced between atomic weights and specific gravities. As regards solids, the researches of Schröder and Kapp seem to suggest that in isomorphous groups the atomic volume (that is, the atomic weight divided by the specific gravity) gives approximately the same results. As regards liquids the subject is involved in even still greater obscurity.

In the case, however, of *both simple and compound gases* the relationship is definite, and obedient to fixed rules :—

(*a.*) *In the case of elementary gases and vapors. The atomic weights* of the elements, we have said, represent *equal volumes* of the elements at the same temperature and pressure. Thus, if $\boxed{\mathrm{H}} = 1$; then $\boxed{\mathrm{O}} = 16$ and $\boxed{\mathrm{N}} = 14$. Or, to state the same truth in another way, 1 grain of hydrogen, 16 grains of oxygen, and 14 grains of nitrogen occupy, temperature and pressure being uniform, 46·663 cubic inches. If, then, we regard hydrogen as 1, and employ it as our standard of comparison, it is manifest that *the atomic weights* of the elementary gases and vapors are also *their relative weights*, hydrogen being regarded as the standard of comparison.

But in stating specific gravities, air, and not hydrogen, constitutes the standard of comparison, it being regarded as equal to 1. Air having a specific gravity of 1, hydrogen is found to have a specific gravity of 0·0693 ; that is, the specific gravity of air as compared to hydrogen is as 1 to 0·0693. Therefore, to find the specific gravity of any elementary gas or vapour, all that is necessary is to multiply its atomic weight by 0·0693, the specific gravity of hydrogen. For example—

To find the specific gravity of oxygen, chlorine, and nitrogen :

0·0693 × 16 (atomic weight of oxygen) = 1·1088, Sp. Gr. of oxygen.
0·0693 × 35·5 („ of chlorine) = 2·4601, „ of chlorine.
0·0693 × 14 („ of nitrogen) = 0·9702, „ of nitrogen.

There are the following *exceptions* to be noted to this rule—

(1.) The vapour densities of *phosphorus and arsenic* compared to hydrogen are twice their atomic weights ; therefore, in estimating the specific gravities of these bodies the atomic weights must be doubled—

31 = atomic weight of phosphorus ; 0·0693 × (31 × 2) = 4·296, Sp. Gr. of phos. vapour.
75 = „ of arsenic ; 0·0693 × (75 × 2) = 10·395 „ of arsenic „

(2.) The vapour densities of *mercury, zinc, and cadmium* compared to hydrogen, are one-half their atomic weights ; therefore, in estimating the specific gravity of these bodies the atomic weights must be halved—

200 = atomic weight of mercury; $0{\cdot}0693 \times \left(\frac{200}{2}\right) = 6{\cdot}93$ Sp.Gr. of mercury vapor.

112 = „ of cadmium; $0{\cdot}0693 \times \left(\frac{112}{2}\right) = 3{\cdot}8808$ Sp.Gr. of cadmium „

(β.) *In the case of compound gases and vapors.*—The molecule of a compound body, it must be remembered, is always twice that of the hydrogen atom. Therefore—

$$\frac{\text{Molecular weight} \times 0{\cdot}0693}{2} \text{ or Relative weight} \times 0{\cdot}0693 = \text{Sp. Gr.}$$

Examples:

HCl; $\frac{0{\cdot}0693 \times 36{\cdot}5\ (HCl)}{2} = 1{\cdot}2647$ Sp. Gr. of hydrochloric acid gas.

H_2O; $\frac{0{\cdot}0693 \times 18\ (OH_2)}{2} = 0{\cdot}6237$ Sp. Gr. of water gas.

H_3N; $\frac{0{\cdot}0693 \times 17\ (NH_3)}{2} = 0{\cdot}5890$ Sp. Gr. of ammonia gas.

CO_2; $\frac{0{\cdot}0693 \times 44\ (CO_2}{2} = 1{\cdot}5246$ Sp. Gr. of carbonic acid gas.

Exceptions in the case of certain bodies must be noted :—

Ammonic chloride (NH_4Cl) has a vapour density of 0·89 (air = 1), This corresponds to the formula $N_{\frac{1}{2}}H_2Cl_{\frac{1}{2}}$.

Phosphoric chloride (PCl_5) has a vapor density of 3·65. This corresponds to the formula $P^{\frac{1}{2}}Cl^{\frac{5}{2}}$.

Ammonic carbamate ($N_2H_6CO_2$) has a vapor density of 0·89. This corresponds to the formula $N_{\frac{2}{3}}H_2C_{\frac{1}{3}}O_{\frac{2}{3}}$.

These three bodies, however, undergo dissociation or partial decomposition when volatilized, NH_4Cl breaking up into $NH_3 + HCl$, PCl_5 into $PCl_3 + Cl_2$, and $N_2H_6CO_2$ into $(NH_3)_2 + CO_2$. Thus the experimental vapor densities must be considered in relation to dissociation. It is worth noting that the products of dissociation in the three cases named recombine on cooling, a circumstance that has not lessened the difficulty of these exceptions. (Page 15.)

Relation between Atomic Weights and Specific Heats.—"*Specific heat*" is the "*quantity of heat*" that a body gives out or takes in, whilst passing from one temperature to another. This is ordinarily determined by estimating the quantity of heat required to raise equal weights of bodies to a given temperature.

For comparison, the standard adopted is *the quantity of heat required to raise* 1 *grm. of water from* 0° *to* 1° C.

This 1 grm. of water is called "*the unit of weight*," and the 1° C. is called "*the unit of heat*" or "*thermal unit.*" It is clear, therefore, that to raise 1 grm. of water from 0° C. to 100° C., or 2 grms. of water from 0° to 50° C. would respectively require 100 units of heat.

Water is chosen for purposes of comparison, because (excepting hydrogen) it requires more heat to raise its temperature than any other known substance.

When we say, therefore, that the specific heat of iron is equal to 0·1138 and that of hydrogen to 3·4090, we imply that if it would take—

1·000 unit of heat to raise 1 grm. of water 1° C. ; it would require
0·1138 „ „ 1 grm. of iron 1° C. ; or
3·4090 „ „ 1 grm. of hydrogen 1° C.

It would seem that the capacities for heat of the atoms of different elements in the solid state are equal, for it is found that although the numbers obtained as the specific heats of different bodies are dissimilar, there is a marked uniformity in the products of the specific heats of bodies when multiplied by their several atomic weights. This number is termed the *atomic heat* of the body, and in the case of the elementary bodies commonly varies between 6 and 7. Probably this slight want of uniformity depends on inaccurate determinations of specific heat. The important influence of specific heat in controlling and determining the atomic weights will be evident.

SPECIFIC HEATS OF CERTAIN ELEMENTARY BODIES.

Elements.	Specific Heat. (Water = 1).	Atomic Weights.	Atomic Heat (Sp. Heat × At. Weight.)
Lithium	0·94	7·	6·6
Sodium	0·29	23·	6·7
Aluminium	0·21	27·	5·7
Phosphorus	0·17	31·	5·3
Sulphur	0·16	32·	5·1
Potassium	0·17	39·	6·6
Iron	0·11	56·	6·2
Nickel	0·10	58·6	6·4
Cobalt	0·10	58·6	6·4
Copper	0·094	63·2	5·9
Zinc	0·094	65·3	6·1
Arsenic	0·081	75·	6·1
Selenium	0·075	79·	5·9
Bromine (solid)	0·084	80·	6·7
Palladium	0·0593	105·7	6·2
Silver	0·056	107·7	6·0
Cadmium	0·0567	112·	6·35
Indium	0·0570	113·4	6·46
Tin	0·0562	118·	6·63
Antimony	0·051	120·	6·1
Iodine	0·0541	127·	6·87
Tellurium	0·0474	128·	6·06
Gold	0·0324	196·	6·3
Mercury	0·0319	200·	6·4
Thallium	0·034	204·	6·9
Lead	0·0314	206·5	6·4
Bismuth	0·031	208·2	6·4

It will be seen that the specific heats of these several bodies multiplied by their atomic weights, produce an almost constant product. We may conclude from this that probably all atoms require the same amount of heat to raise their temperature one degree. This result accords with the surmises of Dulong and Petit, who thought that the atoms of all elementary bodies had the same atomic weight.

Thus far the law may be stated as follows : "*The specific heats of elementary bodies is inversely as their atomic weights.*

There are some apparent *exceptions*. The results, however, obtained by Professor Weber, point to the fact that at high temperatures some at least of the exceptions obey the law of Dulong and Petit. ("Quarterly Journal of Science," Jan., 1876.)

Newman, in 1831, showed that the specific heats of *compound* bodies of similar atomic composition and constitution also vary inversely as the atomic weights—in fact that similar compounds have the same molecular heats, "molecular heat" being the product of molecular weight multiplied by specific heat. Thus—

	Mol. Weight.	Specific Heat.	Mol. Heat.
Chloride of Lithium	42·5	0·2821	12·
Chloride of Sodium	58·5	0·2140	12·5
Chloride of Potassium	74·5	0·1730	12·9
Chloride of Silver	143·2	0·0911	13·0

Further, it would appear that in many cases, although not without exception, the molecular heat of a compound body is the sum of the atomic heats of its constituent elements.

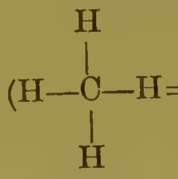
Of Dulong and Petit's law regarding atomic heat the exceptions are mostly in the case of the elements of low atomic weight and low atomic volume, whilst in Newman's law regarding molecular heat, the rule is less certain, and is specially variable where the number of atoms in the molecule is large.

Relation between molecular weight and boiling point.—Such relationship can scarcely as yet be regarded as proved. At any rate, if there seems to be a law for a series, or for a few terms of one series, it does not apply beyond it. It has been shown, however, that for every difference of CH_2 in the lower terms of the normal alcohols of $C_nH_{2n+1}HO$ formula, a difference of 19·5° C. occurs per term in the boiling point, whilst for every difference of CH_2 in the lower terms of the normal fatty acids of the formula C_nH_{6n+1} (COOH), the difference is about 22° C.

Atomicity or Quantivalence.—The terms *quantivalence* (*quanti* and *valeo*), *dynamicity*, or *atomicity* imply, that although the symbol of an element (such as O, N, etc.), represents an atom of that element, the atom having an unchangeable *relative* weight (for of the *absolute* weights of the atoms we know nothing with certainty), nevertheless, that such symbol does not express "the *valence*," or "*chemical value*" of such atom, this power varying with different bodies.

Thus in *hydrochloric acid* (HCl), one chlorine atom is satisfied with (has one point of attraction for, or, in other words, has the same value as), one hydrogen. Under no circumstances can one of chlorine combine with more than one of hydrogen. But in water (H_2O) we find that one oxygen atom is not satisfied with less than than 2 of hydrogen, whilst in marsh gas (CH_4) one carbon atom is not satisfied with less than 4 of hydrogen. Thus it is evident that the power of carbon, as represented by the symbol C, is chemically equal to 4 hydrogens, the symbol O to 2 hydrogens, and the symbol Cl to 1 hydrogen. The terms *quantivalence*, *dynamicity*, or *atomicity* express, therefore, the fact that an atom of one element may be chemically equal to, and have the power of fixing, one or more atoms of other elements.

The value or atomicity of elements is often represented by lines or bonds, expressive of what Frankland calls its atom-fixing power.

Thus, $Cl—$, $—O—$, $—\overset{|}{\underset{|}{C}}—$, represent graphically chlorine as a monad with one bond, oxygen as a dyad with two bonds, and carbon as a tetrad with four bonds. Chlorine, we know, can only fix one atom of hydrogen to form a molecule of HCl (thus $Cl—H=HCl$), whilst oxygen can fix two hydrogen atoms to form a water molecule ($H—O—H=OH_2$), and carbon can fix four hydrogen atoms to form a marsh gas molecule  $(H—\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}—H=CH_4)$ (graphic formulæ). Thus the lines are graphic expressions of the atomicity of a body, and are to be regarded as pictures representing the number of bonds, and how they are severally utilised. Graphic formulæ, however (like symbolic formulæ), convey no indication of potential energy.

No element can exist with its bonds unconnected or dissatisfied. It is clear, therefore, that the molecule of any element possessing an uneven number of bonds (*i.e.*, being a perissad) must consist of two or more atoms united. You cannot have hydrogen in a free state thus $—H$; but you can have it thus, $H—H$. Hence we regard H_2 as the hydrogen molecule, and not H. In the case of an *artiad*, *i.e.*, an element possessing an even number of bonds, it is possible to conceive the molecule to consist of one atom (*monatomic*), inasmuch as the bonds, by combining amongst themselves, may satisfy each other, and so become latent.

Glyptic formulæ are merely material illustrations of graphic formulæ, where atoms are represented by balls, and lines by wires.

Method of Determining the Quantivalence or Atomicity of a Body.

Agreeing to understand by the quantivalence of a body, the number of univalent atoms with which the symbol representing its atomic weight may unite, we determine this quantivalence in such ways as the following :—

(1.) *By the number of hydrogen atoms with which a body can combine to form a molecule.*

Example. 1 of hydrogen combines with 1 of chlorine. Therefore the valence of chlorine = the valence of hydrogen.

(2.) *If an element will not combine with hydrogen, but will combine with chlorine, its valence may then be determined by the number of chlorine atoms with which it will combine to form a molecule.*

Example. 1 atom of silver (Ag) combines with 1 atom of chlorine, and in that proportion only. But silver will not combine with hydrogen. Inasmuch, however as 1 of chlorine combines with 1 of hydrogen, and 1 of chlorine with 1 of silver, we infer that if silver could be made to combine with hydrogen, it would do so in the proportion of 1 atom of hydrogen to 1 atom of silver. We may express these facts thus—

(1) The valence of silver = the valence of chlorine;
(2) The valence of chlorine = the valence of hydrogen ;
Therefore (3) The valence of silver = the valence of hydrogen.

It will thus be seen that hydrogen, chlorine, and silver are, so far as atomicity is concerned, equivalent.

(3.) *By the proportion of hydrogen a body is capable of replacing in a saline molecule.*

Examples. (*a.*) A water molecule is made up of 2 atoms of hydrogen and 1 of oxygen. One or both of the hydrogen atoms may be replaced by an alkaline metal, such as potassium. Thus—

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O = H_2O;\quad \left.\begin{matrix}H\\K\end{matrix}\right\}O = KHO;\quad \left.\begin{matrix}K\\K\end{matrix}\right\}O = K_2O.$$

It is clear, therefore, that the value (or valence) of potassium is identical with that of hydrogen.

(*b.*) Again: calcium, zinc, or barium may also be made to take the place of hydrogen, but under such circumstances it will be found that 1 atom of these elements is equivalent to 2 atoms of hydrogen. Thus:—

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O = H_2O\ ;\quad Ca''O\ (\text{not } Ca_2O);\quad Zn''O\ (\text{not } Zn_2O).$$

Hence, the valence of calcium or of zinc is double that of hydrogen, inasmuch as 1 of zinc or 1 of calcium can replace 2 of hydrogen in a molecule.

Looking, therefore, at these facts, it is clear that the elements have very different values in their capacities for substitution displacement. Agreeing to regard hydrogen as our standard unit of atomicity, it is evident that the elements are susceptible of arrangement into groups, as follows:—

Group I.

Univalent elements; that is, 1 atom in chemical exchange is equal in value to 1 atom of *hydrogen* or other univalent element. Such bodies are called *monad elements.*

Group II.

Divalent elements; that is, 1 atom in chemical exchange is equal to, and may replace, either (*a*) 2 atoms of hydrogen, or 2 atoms of any other monad; or (*b*) 1 atom of any other divalent element. Such bodies are called *dyad elements.*

Group III.

Trivalent elements; that is, 1 atom in chemical exchange is equal to (*a*) 3 atoms of hydrogen or other monad element; or to (*b*) 1 atom of a divalent element + 1 atom of a monad element. Such bodies are called *triad elements.*

Group IV.

Quadrivalent elements; that is, 1 atom in chemical exchange is equal to (*a*) 4 atoms of hydrogen or other monad element; or to (*b*) 2 atoms of oxygen or other dyad element; or to (*c*) 1 atom of a dyad + 2 atoms of a monad element; or to (*d*) 1 atom of a triad + 1 atom of a monad element. Such bodies are called *tetrad elements.*

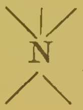
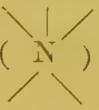
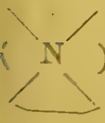
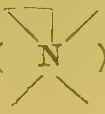
Groups V., VI., VII., VIII., ETC.

Quinquivalent, hexivalent, etc., elements; that is, 1 atom in chemical exchange is equal to 5, 6, or more atoms of hydrogen or their equivalent respectively.

We borrow the following diagram, representing the atomicity of the elements, from Frankland and Japp's "Chemistry." The non-metals are printed in thick type, and the metals in ordinary Roman type:—

TABLE OF ATOMICITIES.

Monads.	Dyads.	Triads.	Tetrads.	Pentads.	Hexads.	Heptads.	Octads.
I. **Hydrogen.**	I. **Oxygen.**	I. **Boron.**	I. **Carbon.** **Silicon.** Tin. Titanium. Thorium. Zirconium.	I. **Nitrogen.** **Phosphorus.** Vanadium. Arsenic. Antimony. Bismuth. Niobium. Tantalum.	I. **Sulphur.** **Selenium.** **Tellurium**	I. **Chlorine.** **Bromine.** **Iodine.** Usually regarded as monads.	I. Ruthenium Osmium.
II. **Fluorine.** **Chlorine.** **Bromine.** **Iodine.**	II. Barium. Strontium. Calcium. Magnesium Zinc. Beryllium.	II. Gold.	II. Gallium. Aluminium	II. Didymium.	II. Uranium. Tungsten. Molybdenum.		
III. Cæsium. Rubidium. Potassium. Sodium. Lithium.	III. Cadmium. Mercury. Copper.	III. Thallium. Indium.	III. Cerium.		III. Chromium. Manganese. Iron. Cobalt. Nickel.		
IV. Silver.		IV. Lanthanum Yttrium. Erbium. Decipium. Samarium. Scandium.	IV. Platinum. Iridium. Palladium. Rhodium.				
			V. Lead.				

Although we arrange elements in their several classes according to their values as best we know them, it must not be supposed that atomicity is a fixed quantity. *The valence of an element may vary: Carbon*, for example, in marsh gas is a tetrad ($C^{iv}H_4$). So also it is quadrivalent in carbonic anhydride ($C^{iv}O_2$), whilst in carbonic oxide ($C''O$) it plays the part of a dyad. *Nitrogen*, again, may act as a monad, as in N_2O, or as a triad, as in NH_3, or as a pentad, as in NH_4Cl. Admitting that these variations are difficult of explanation and somewhat interfere with general conclusions, we may note, as Dr. Frankland remarks, that the variation always takes place by the disappearance or development of an even number of bonds. Thus nitrogen may be a monad ($-N$), a triad ($-\overset{|}{N}-$), or a pentad (); it is never a dyad, or a tetrad. Carbon may be a dyad ($-C-$), or a tetrad ($-\underset{|}{\overset{|}{C}}-$), but it is never a monad or a triad. In short, a perissad is never an artiad, nor an artiad a perissad. Dr. Frankland explains these variations by supposing that some of the bonds unite, and, having saturated each other, become latent. Thus nitrogen with its five bonds () becomes a triad by the union of two; thus (), or a monad by the union of four (). In this way

Frankland distinguishes between *latent atomicity*, or the number of conjoined bonds; *active atomicity*, or the total number of bonds in actual combination with other elements; and *absolute atomicity*, the sum of the latent and the active atomicities. Whenever an element is fully saturated, that is, has received its full value of other elements, the body so formed is more stable than when its valence is not fully satisfied. Hence the true valence of an element is always indicated by the largest number of hydrogen or other monad elements with which it can combine. The valence, moreover, must not be determined from oxides or from sulphides, because each dyad, made up as it is of two units of equivalency, neutralises one unit in the compound it enters, and, by introducing a second unit, leaves the equivalence as it was before.

For convenience these several groups are divided under the two heads of *Odds* and *Evens*:—

(1.) *Odds* or *Perissads* (περισσὸς, odd)	Monads.
	Triads.
	Pentads.
	Heptads
(2.) *Evens* or *Artiads* (ἄρτιος, even)	Dyads.
	Tetrads.
	Hexads.
	Octads.

The quantivalence of bodies is usually denoted by placing dashes or Roman figures to the right of the symbol. Thus, H' with one dash means that hydrogen is a monad; O'' with two dashes, that oxygen is a dyad; while C^{iv} shows carbon to be a tetrad, and so forth.

The Periodic Law.—In 1864, Newlands, under the phrase "Law of Octaves," suggested that the properties of elementary bodies varied periodically with their atomic weights. In 1869 Mendeleef gave greater precision to this idea of periodicity, formulating the general law that "*The properties of the elements are a periodic function of their atomic weights.* Further, he extended the application of the law to the correction of doubtful atomic weights and the prediction of new elements.

Mendeleef's table is as follows:—

THE PERIODIC SYSTEM OF THE ELEMENTS (MENDELEEFF.)

Groups:	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Series:	— R_2O	— R_2O_2	— R_2O_3	RH_4 R_2O_4	RH_3 R_2O_5	RH_2 R_2O_6	RH R_2O_7	(R_2H) (R_2O_8)
1 2	1 H Li 7	— Be 9	— B 11	— C 12	— N 14	— O 16	— F 19	— —
3 4	23 Na K 39	24·4 Mg Ca 40	27 Al Sc 44	28·2 Si Ti 48	31 P V 51·3	32 S Cr 52	35·5 Cl Mn 55	Fe 56, Co 58·6, Ni 58·6
5 6	63·2 Cu Rb 85·3	65·3 Zn Sr 87·5	68·8 Ga Y 89·8 ?	72 ? Zr 90	75 As Nb 94	79 Se Mo 95·5	80 Br ? 100	Ru 104, Rh 104, Pd 105·7
7 8	107·7 Ag Cs 133	112 Cd Ba 137	113·4 In La 138·5	118 Sn Ce 140·5	120 Sb Di 146	125 Te Tb? 148·8	127 I Sm? 150	? 152, ? 153, ? 154
9 10	156 ? ? 170	158 ? ? 172	159 Dp? Yb 172·8	162 ? ? 177	165·9 Er? Ta 182	167 ? W 184	169 ? ? 190	Os 198·6 ?, Ir 192·5, Pt. 194·4
11 12	196 Au ? 221	200 Hg ? 225	204 Tl ? 230	206·5 Pb Th 233·4	208·2 Bi ? 237	214 Ng ? U 238·5	219 ? ? 244	

It will be seen that the elements are arranged, in the order of their atomic weights, in horizontal lines. Each horizontal line is numbered with Arabic numbers (1, 2, 3, etc.), and is termed a "series" or "period." No special similarity of property is apparent between the various elements of one series or period arranged on a single horizontal line, such as, for example, those on line 2, which includes lithium, beryllium, boron, carbon, nitrogen, oxygen, and fluorine. But having thus tabulated the whole of the elements in twelve horizontal lines, from left to right, a well-marked relationship will be noted when we compare together the elements that arrange themselves in the eight vertical columns. Each vertical column is numbered with a Roman number (I., II., III., etc.), and is termed a "group" or "family." Thus, lithium, sodium, potassium, rubidium, cæsium, which occur in the first vertical column (Group I.), or magnesium, calcium, strontium, barium, which occur in the second column (Group II.), are, respectively, closely allied elements. Thus it would seem that there is a periodic variation, the like changes of character that occur in the elements in one horizontal line being repeated in each of the remaining horizontal lines.

Mendeleef further points out that there are two kinds of periods. the one following the even Arabic numbers of his table, and the other the odd. For example, in Group II. beryllium, calcium, strontium, and barium belong to the even-numbered series (2, 4, 6, and 8), whilst magnesium, zinc, cadmium, and mercury belong to the odd-numbered series (3, 5, 7, and 11). Thus, he subdivides and differentiates the properties of the members of his primary groups.

Some few further points must be noted—

(1.) That the quantity of oxygen with which the several groups can unite increases group by group. Thus, in Group I., R_2O ; in Group II., R_2O_2 ; in Group III., R_2O_3, etc., represent the several oxides of the groups.

(2.) That as the groups progress there is an increase in the quantivalence of the elements falling within it, Group I. being composed of monads, Group II. of dyads, &c. As a result, odd and even atomicity alternate group by group.

(3.) That in Group VIII. three elements occur. These are termed by Mendeleef "transitional elements," that is, elements occurring between the even and the odd series of a long period. They are all of even atomicity, but their atomicity decreases with the rise of atomic weight.

(4.) That the law of periodicity *quâ* chemical properties, is also true *quâ* the physical properties, of the elements (noted by Lothar Meyer). Two examples may be given—

(*a.*) The para-magnetic elements, that is, the elements attracted by a magnet (viz., K, C, Ti, Ce, N, O, Cr, U, Mn, Fe, Co, Ni, Rh, Pd, Os, Ir, and Pt) are found in the even series or periods of the table, 2, 4, 6, &c., whilst the dia-magnetic elements, that is, the elements repelled by a magnet (viz., H, Na, Cu, Ag, Au, Zn, Cd, Hg, Tl, Si, Sn, Pb, P, As, Sb, Bi, S, Le, Cl, Br, I), are found in the odd series or periods, 1, 3, 5, etc., of the table.

(β.) Traversing a series or period from left to right, a gradation of stages will be noted, from the most electro-positive element to the most electro-negative.

The value of this law of periodicity is more particularly to be seen in two directions—

(α.) In the prediction of new elements. This results from observing the gaps that occur in the tabulated arrangement. Thus, in Group III., 5, Mendeleef predicted an element (which he named EK-aluminium) having an atomic weight about 68, a specific gravity of 6, and capable of forming a sesquioxide (R_2O_3). The discovery of gallium confirmed his prophecy.

(β.) By correcting doubtful atomic weights. This results from a want of harmony (*i.e.*, that the groups do not coincide accurately with the series) being apparent in the periods. Thus recalculations of the atomic weights of indium, uranium, molybdenum, and tellurium were suggested by Mendeleef, and his predictions respecting them were for the most part confirmed. (*See* Index for these elements.)

The law of periodicity is still hypothetical ; special care is needed when a consistent table becomes a necessary part of an argument. As yet there are some difficulties to be overcome. Beryllium, *e.g.*, all experiments prove, has an atomic weight of 13·6, and not of 9, as is shown in Mendeleef's table.

Chemical Formulæ.

The object of chemical formulæ is to express the composition and the probable constitution of a chemical substance. Formulæ are of two kinds—

(1.) *Experimental or empirical.*
(2.) *Theoretical or rational.*

I. EXPERIMENTAL OR EMPIRICAL FORMULÆ.

An empirical formula represents merely by the smallest integers the number of atomic proportions of the several elements present in a body. It is the expression of the actual experimental results of analysis. An empirical formula in no way represents the groupings of the elements. We give, as an illustration, the determination in detail of the empirical formula for magnesic sulphate.

(1.) *Determine the percentage composition.* On analysis, we should find in every 100 parts of magnesic sulphate—

Magnesic oxide (magnesia) ...	16·26
Sulphuric anhydride	32·52
Water	51·22=100·00

(2.) *Divide the numbers thus obtained* (*i.e.*, the percentage numbers) *severally by their atomic weights.* Thus, 40, 80, and 18 represent respectively the atomic weights of magnesia, sulphuric anhydride, and water. Therefore—

$$\frac{16{\cdot}26}{40}={\cdot}4065; \qquad \frac{32{\cdot}52}{80}={\cdot}4065; \qquad \frac{51{\cdot}22}{18}=2{\cdot}845.$$

(3.) *Reduce the quotients to their simplest expression.* Thus—

	Magnesia.	Sulphuric anhydride.	Water.
The ratio of the numbers	0·4065	0·4065	2·845
corresponds to	1	1	7

From which it is clear that the relative atomic proportion of magnesia (MgO) to sulphuric anhydride (SO_3) is as 1 to 1, and of these to water (H_2O) as 1 to 7. Thus, $MgO+SO_3+H_{14}O_7$ or $MgSO_{11}H_{14}$ represents the experimental or empirical formula for magnesic sulphate. Hence the rules to determine the empirical formula of a body may be thus summarised—

(1.) Determine by analysis its percentage composition.
(2.) Divide the numbers so obtained by their atomic weights.
(3.) Reduce the quotients to their simplest expression.

II. RATIONAL OR THEORETICAL FORMULÆ.

Such formulæ represent not only the elements present and their atomic proportions, but the manner (according to every man's views or fancies) in which the elements are grouped. Thus, magnesic sulphate may be written $MgO, SO_3, 7H_2O$, or $MgSO_4, H_2O, 6H_2O$, and in many other ways. It may be judged, if different opinions exist as to the exact method of expressing the theoretical formula of so simple a body as magnesic sulphate, what a play there is for imagination in the expression of the formulæ of complex organic bodies. For example, there are nineteen different ways of representing acetic acid ($C_2H_4O_2$). Such formulæ are as yet merely *theoretical.*

Frankland has suggested the use of what he calls *constitutional formulæ,* with the notion of giving some idea of the arrangement of atoms in a molecule. In a constitutional formula the symbol of the principal element is placed first, thereby denoting that the several elements, or compound radicals following it on the same line, are held to it, as the principal element of the molecule, by what Frankland terms bonds. We may regard the molecule in this sense as a family, and the principal element as the parent or head of the family. Further, to distinguish constitutional formulæ from molecular or empirical formulæ, the head of the family, or the principal bondholder or bondholders are printed in thick type.

Substitution (*Substitutus,* put in another's place).

(A.) **Inorganic.**—Having regard to the molecular constitution of matter, we find that, in mineral chemistry, the several constituents of a molecule may be replaced (*i.e.* substituted) by their equivalent of other bodies, without changing the typical constitution of the original molecule. Thus—

(1.) $\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}$ represents a molecule of *hydrogen.*

(*α.*) One hydrogen atom (monad) of this *hydrogen* molecule may be replaced by a haloid atom (monad) to form the hydracids; thus—

$$HH;\ HCl;\ HBr;\ HI;\ HF.$$

(*β*). One hydrogen atom may also be replaced by an alkaline metal, to form a hydride.

(2.) $\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\ (=\mathrm{H_2O})$ represents a molecule of *water.*

(*α.*) One or both hydrogen atoms of this *water* molecule may be replaced by an alkaline metal; thus—

$$\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O};\quad \overbrace{\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O};\quad \left.\begin{matrix}\mathrm{Na}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O};}^{\text{Hydrates.}}\quad \overbrace{\left.\begin{matrix}\mathrm{K}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O};\quad \left.\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\right\}\mathrm{O}.}^{\text{Oxides.}}$$

(*β.*) Two hydrogen atoms may be replaced by one of a dyad element; thus—

$$\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O};\quad \mathrm{Zn''O};\quad \mathrm{Ca''O};\quad \mathrm{Ba''O}.$$

(*γ.*) The dyad oxygen may be replaced by the dyads sulphur, selenium, or tellurium; thus—

$$\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O};\quad \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S};\quad \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{Se};\quad \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{Te}.$$

(3.) $\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}\ (=\mathrm{NH_3})$ represents a molecule of *ammonia.*

(*α.*) The three hydrogen atoms of this *ammonia* molecule may be replaced by three chlorine, bromine, or iodine atoms; thus—

$$NH_3;\ NCl_3;\ NBr_3;\ NI_3.$$

(*β.*) A part only of the hydrogen may be replaced by a metal, or by a compound radical; thus—

NH_3; NH_2K (Potassamide); $(SO_2(NH_2)_2)$ (Sulphamide).

(γ.) The nitrogen may be wholly or partially replaced by phosphorus, arsenic, antimony, and perhaps by bismuth.

(4). $\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C\ (=CH_4)$ represents a molecule of *marsh gas.*

Here substitutions are endless, as we shall note more particularly under organic chemistry.

(5.) In the formation of salts, the hydrogen of an acid is replaced by one or more atoms of a metal or compound positive radical; thus—

(a.) *Sulphuric acid* contains two displaceable atoms of hydrogen (H_2SO_4).

1 hydrogen	may be displaced by	1 of potassium	(monad)	forming	$HKSO_4$ (*acid salt.*)
2 hydrogens	„ „	2 of „	(„)	„	K_2SO_4 (*normal salt.*)
2 hydrogens	„ „	1 of calcium	(dyad)	„	$CaSO_4$

(β.) *Phosphoric acid* contains three displaceable atoms of hydrogen (H_3PO_4).

3 hydrogens	may be displaced by	3 of silver	(monad)	Ag_3PO_4
2 „	„	2 of sodium	(„)	HNa_2PO_4
1 „	„	1 of „	(„)	NaH_2PO_4

Similarly, 1 triad will take the place of 3 monads, or 1 dyad of 2 monads.

(B.) **Organic.**—The substitution of compound radicals for elements, forms a remarkable feature in organic chemistry. Liebig defined organic chemistry as "*the chemistry of compound radicals.*"

(1.) One of the hydrogen atoms of a hydrogen molecule (HH) may be replaced by such compound radicals as Methyl (CH_3), Ethyl (C_2H_5), Propyl (C_3H_7), etc., whereby a hydride of the organic radical is formed. Thus—

$(CH_3)H =$ *Methyl-hydride*; $(C_2H_5)H =$ *Ethyl-hydride*; $(C_3H_7)H =$ *Propyl-hydride.*

Further, the hydrogen of these compounds may be replaced by chlorine or cyanogen. Thus —

$(CH_3)Cl =$ *Methyl-chloride*; $(C_2H_5)Cl =$ *Ethyl-chloride*; $(C_3H_7)Cl =$ *Propyl-chloride.*
$(CH_3)Cy =$ *Methyl-cyanide*; $(C_2H_5)Cy =$ *Ethyl-cyanide*; $(C_8H_7)Cy =$ *Propyl-cyanide.*

(2.) In the alcohols and ethers, we find bodies constructed on the water (H_2O) type.

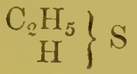
(a.) One hydrogen of a water molecule may be replaced by a compound radical to form an *alcohol*; thus—

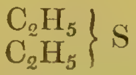
$$\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O = \textit{Methyl alcohol}; \quad \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O = \textit{Ethyl alcohol.}$$

(β.) Both atoms of hydrogen may be replaced by two of the compound radical to form an *ether*; thus—

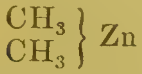
$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O = \textit{Methyl ether}; \quad \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O = \textit{Ethyl ether.}$$

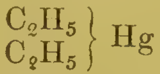
(γ.) Or the oxygen may be replaced by sulphur, and perhaps by selenium; thus—


$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S = \text{Ethylic sulphydrate};$$
(Mercaptan.)


$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S = \text{Ethylic sulphide.}$$
(Sulphur ether.)

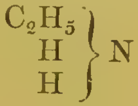
(δ.) Or the oxygen may be replaced by silicon or by a metal, whereby the metallic ethyls, etc., are produced; thus—

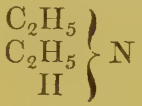

$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}Zn = \text{Zincic methide.}$$

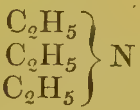

$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Hg = \text{Mercuric ethide.}$$

(3.) Bodies constructed on the ammonia (NH_3) type are found in the amides and in the alcoholic ammonias.

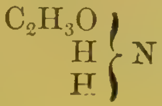
(α.) One or more atoms of hydrogen may be replaced by one or more compound radicals, such as ethyl (C_2H_5); thus—

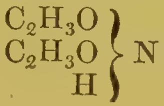

$$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N = \text{Ethylamine};$$

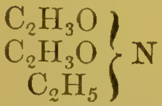

$$\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N = \text{Diethylamine};$$


$$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N = \text{Triethylamine.}$$

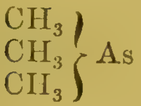
(β.) One or more atoms of hydrogen may be replaced by an oxydized radical, as in the "amides," or else by different radicals; thus—

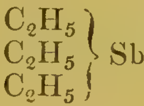

$$\left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N = \text{Acetamide};$$
(called a primary amide.)

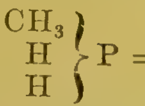

$$\left.\begin{matrix}C_2H_3O\\C_2H_3O\\H\end{matrix}\right\}N = \text{Diacetamide};$$
(called a secondary amide.)


$$\left.\begin{matrix}C_2H_3O\\C_2H_3O\\C_2H_5\end{matrix}\right\}N = \text{Ethylic Diacetamide.}$$

(γ.) The nitrogen may be replaced by arsenic, antimony, bismuth, etc., as follows:—


$$\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}As = \text{Trimethyl-arsine};$$


$$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}Sb = \text{Triethyl-stibine};$$


$$\left.\begin{matrix}CH_3\\H\\H\end{matrix}\right\}P = \text{Methyl-phosphine.}$$

(4.) In the case of the marsh gas (CH_4) molecule, the substitutions are without number, the hydrogens being replaced in almost endless variety.

Isomerism (*ἴσος* equal, *μέρος* a part).

Isomerism is a term applied to bodies containing the same elements, united in the same proportions, but differing more or less widely in their physical, physiological, and chemical properties.

Isomerides are of two classes:—

(1.) Where the *percentage* composition is similar, but the *molecular* composition dissimilar (polymers);

(2.) Where both percentage and the molecular composition are alike (metamers).

I. *Isomerides having similar percentage but different molecular composition; in other words, having different vapor densities* (Polymerism). Examples of such isomerides (polymers) are seen in the following cases :—

(*a.*) *Cyanogen* (CN or Cy), a poisonous gas, and *Paracyanogen* (C^nN^n or $\bar{Cy}^n$), an inert solid, alike contain in every 100 parts—

Carbon 46·15 ; nitrogen 53·85.

(*β.*) *The chlorides of Cyanogen, viz.:*—

$CyCl$ = gaseous chloride of cyanogen.
Cy_2Cl_2 = liquid " "
Cy_3Cl_3 = solid " "

have a similar percentage composition, viz. :—

Carbon, 19·51 ; nitrogen, 22·77 ; chlorine, 57·72.

Further illustrations of polymerism may be found in the cyanogen oxyacids (viz., cyanic, fulminuric, and cyanuric acids, and cyamelide) ; also in the various hydrocarbon series, and in numerous other cases.

II. *Isomerides having an identical percentage and molecular composition* (Metamerism). These bodies, consequently, have similar vapor densities. Examples of such isomerides (metamers) are seen in the following cases :—

(*a.*) *Urea* [$(2NH_2)CO$] and *ammonic cyanate* [$CN(NH_4O)$], both of which are represented by the formula CH_4N_2O, contain in every 100 parts—

Carbon...	20·00
Hydrogen	6·67
Nitrogen	46·66
Oxygen	26·67=100·00

(*β.*) The "*turpenes*" (including oils of turpentine, lemons, bergamot, neroli, lavender, pepper, camomile, carraway, cloves, etc.), have all a similar composition ($C_{10}H_{16}$).

(*γ.*) *Tartaric acid* (which turns the plane of polarized light to the right, and is hence called dextro-tartaric acid), *racemic acid* (which has no action on a ray of polarized light), and *paratartaric acid* (which turns the ray to the left, and is hence known as levo-tartaric acid), have a similar percentage and molecular composition ($C_4H_6O_6$).

(*δ.*) *Morphia* (the active principle of opium) and *piperin* (the active principle of pepper) are both represented by the formula $C_{17}H_{19}NO_3$. We may note that these isomerides are divisible into two classes :—

1. *Bodies differing in their physical properties, but behaving alike under the action of chemical reagents.* Such, for example, are the turpenes, a series of true isomerides ; and,

2. *Bodies not only differing in physical properties, but also behaving differently under the action of chemical reagents.*—In such bodies we note the presence of different radicals. For example, propionic acid, methyl

acetate, and ethyl formate are isomeric ($C_3H_6O_2$), but their behaviour respectively with potassic hydrate is vastly different. Thus—

1. Propionic acid with potassic hydrate yields potassic propionate.
2. Methyl acetate ,, ,, potassic acetate and methyl alcohol.
3. Ethyl formate ,, ,, potassic formate and ethyl alcohol.

Isomorphism (ἴσος equal, and μορφή a form).

Isomorphic bodies are those that crystallise in the same form and possess similar constitutions. Thus, lead, barium, and strontium nitrates are isomorphous, the lead, barium, and strontium being "the corresponding elements." It is worth noting, in connection with this fact, that Mendeleef, in his table (see page 53), brings sodium, silver, and copper into one group (II., odd numbers) and that many cuprous and argentic compounds are isomorphous; the same being true of silver and sodium compounds.

Acids may frequently be substituted for acids, and bases for bases, in a body, without the body undergoing any alteration of form. Thus, in common potash-alum ($K_2Al_24SO_4,24H_2O$), the K_2 may be replaced by Na_2, or by $(NH_4)_2$, and the Al_2 by Fe_2, Mn_2, or Cr_2, etc., without any change of form resulting.

It has been suggested (Blake, B. Assoc., 1846) that there is a relationship between the physiological action of bodies and their isomorphism.

Allotropism (ἄλλος another, and τροπή twist or turn).

The capability of *compound* bodies, having the same percentage and molecular composition, of existing in more than one shape, to which we have alluded under the term isomorphism, finds its parallel amongst the *elementary* bodies. Certain polyad elements assume various and well-marked modifications. Berzelius has termed this *allotropism*, which bears the same relationship to the *element* that *isomerism* does to the *compound*. The existence of *carbon* as charcoal, graphite, and the diamond; the varieties of *phosphorus*; *sulphur* in its various modifications, *oxygen* as common oxygen and as ozone, etc., are illustrations of allotropism.

The Metric System (Unit of Length).

The mètre (*unit of length*) is a bar of platinum deposited in the archives of Paris, measuring 39·37 English inches, at 32° F. (0° C.). It is adopted as a measure of length, surface, weight, and capacity.

I. As a Measure of Length (De la Rue).

Its *multiples* are marked by *Greek* prefixes. and its *subdivisions* by *Latin* prefixes.

	In English Inches.	In English Feet.	In English Yards.	In English Miles.
Millimètre	0·03937	0·003281	0·0010936	0·0000006
Centimètre	0·39370	0·032809	0·0109363	0·0000062
Decimètre	3·93708	0·328089	0·1093633	0·0000621
Mètre	39·37079	3·280890	1·0936331	0·0006214
Décamètre	393·70790	32·808992	10·9363310	0·0062138
Hectomètre	3937·07900	328·089920	109·3633100	0·0621382
Kilomètre	39370·79000	3280·899200	1093·6331000	0·6213824
Myriomètre	393707·90000	32808·992000	10936·3310000	6·2138244

1 inch = 2·539954 centimètres.
1 foot = 3·0479449 decimétres.

1 yard = 0·9143835 mètres.
1 mile = 1·6093149 kilomètres.

II.—As a Measure of Surface (De la Rue).

	In English square feet.	In English square yards.	In English acres = 43560 sq. feet.
1 square mètre (Centiare)	10·764299	1·196033	0·0002471
100 square mètres (Are)	1076·429934	119·604326	0·0247114
10,000 square mètres (Hectare)	107642·993418	11960·432602	2·4711431

1 square inch = 6·4513669 square centimètres.
1 square yard = 0·83609715 square mètre.
1 square foot = 9·2899683 square decimètres.
1 acre = 0·40467102 hectare.

III. As a Measure of Capacity (De la Rue).

A cubic decimètre (that is, a cube each side of which measures 3·937 inches) holds a *litre* of water at 4° C. (*i.e.*, the temperature at which water is at its maximum density). This litre weighs 1 kilogramme, or 1,000 grammes. A cubic centimètre, therefore, holds a gramme of water at 4° C.

	In cubic inches.	In cubic feet = 1728 cubic inches.	In pints = 34·65923 cubic inches.	In gallons = 8 pints = 277·27384 cubic inches.	In bushels = 8 gallons = 2218·19078 cubic inches.
Millilitre or a cubic centimètre..	0·06103	0·000035	0·00176	0·0002201	0·0000275
Centilitre or 10 cubic centimètres	0·61027	0·000353	0·01760	0·0022009	0·0002751
Décilitre or 100 cubic centimètres	6 10271	0·003532	0·17607	0·0220096	0·0027512
Litre or cubic decimètre	61·02705	0·035317	1·76077	0·2200966	0·0275120
Décalitre (centistère or 10 litres)	610·27052	0·353166	17·60773	2·2009667	0·2751208
Hectolitre (Decistère or 100 litres)	6102·70515	3·531658	176·07734	22·0096676	2·7512084
Kilolitre or cubic mètre	61027 05152	35·316581	1760·77341	220·0966767	27·5120845
Myriolitre (Décastère)..........	610270 51519	353·165807	17607 73414	2200·9667675	275·1208459

1 cubic inch = 16.386176 cubic centimètres.
100 cubic in. = 0·3606 of gallon.
1 cubic foot = 28·315312 cubic decimètres.
1 gallon = 4·543358 litres = 277·276 c. i.
1 litre = 35·2754 fl. ozs. = 1·76377 pints.
1 pint = 34·659 c. i. = $\frac{1}{8}$ of gallon = 0·5679 litre.
1 fluid oz. = 1·7329 c. i.

IV. As a Measure of Weight.

A cubic centimètre (that is, a vessel, each side of which measures 0·3937 inches) holds a quantity of water which at 4° C. (the maximum density of water) weighs 1 gramme (15·432 grains).

Measures of Weights.

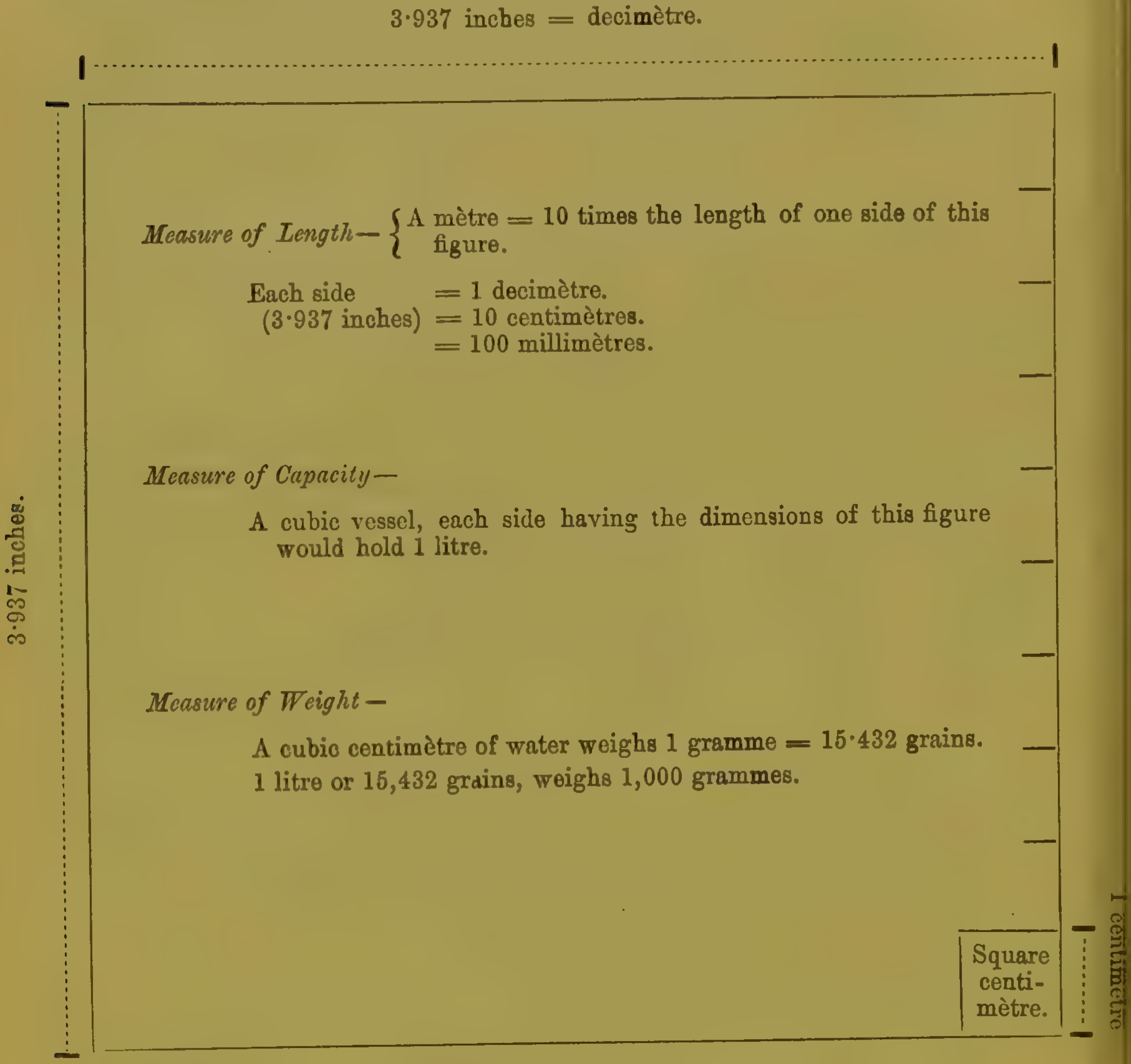
1 cubic inch of distilled water (62° F.) weighs in air 252·456 grains.
1 do. do. do. in vacuo 252·722 grains.

	In grains.	In ounces Troy = 480 grains.	In pounds avoirdupois =7000 grs.	In cwts. = 112 lbs. = 784000 grs.	In tons = 20 cwts. = 15680000 grs.
Milligramme..	0·01543	0·000032	0·0000022	0·0000000	0·000000001
Centigramme..	0·15432	0·000321	0·0000220	0·0000002	0·00000001
Decigramme..	1·54323	0·003215	0·0002204	0·0000019	0·0000001
Gramme	15·43234	0·032150	0 0022046	0·0000196	0·000001
Decagramme..	154·32349	0·321507	0·0220462	0·0001968	0·0000098
Hectogramme.	1543·23488	3·215072	0·2204621	0·0019684	0·0000984
Kilogramme ..	15432·34880	32·150726	2·2046212	0·0196841	0·0009842
Myriogramme.	154323·48800	321·507267	22·0462126	0·1968412	0·0098421

1 grain = 0·064799 grammes.
1 oz. troy =31·103496 grammes.
1 lb. avoirdupois = 0·453495 kilogrammes.
1 cwt. =50·802377 kilogrammes.
1 lb. per sq. inch =0·07 kilos per sq. centim.
1 kilo per sq. millim=1425·45 lbs. per sq. inch.

A kilogramme (=1000 grammes) is about equal to 2¼ lbs. avoirdupois, and 1000 kilogrammes are nearly equal to 1 ton; 1 kilogramme = 35·2739 ozs. avoirdupois, and 2·2046 lbs. avoirdupois.

The following figure represents the metre in its threefold function of a measure of length, capacity, and weight.



Measure of Length— { A mètre = 10 times the length of one side of this figure.

Each side = 1 decimètre.
(3·937 inches) = 10 centimètres.
= 100 millimètres.

Measure of Capacity—

A cubic vessel, each side having the dimensions of this figure would hold 1 litre.

Measure of Weight—

A cubic centimètre of water weighs 1 gramme = 15·432 grains.
1 litre or 15,432 grains, weighs 1,000 grammes.

CHAPTER III.

CRYSTALLIZATION.

Definition of a Crystal—Classification.

A CRYSTAL (κρύσταλλος) is a geometrical solid having a rectilinear structure. The phrase "*crystallized body*" is employed in contradistinction to the phrase "*amorphous body*," such as glass, that is a body devoid of crystalline structure.

The process by which crystals are formed is called crystallization.

The chief processes for obtaining crystals are three :—

1. Solution.
2. Fusion.
3. Sublimation.

By the *faces* of a crystal we imply its plane surfaces ; by the *edges*, the lines formed by the union of contiguous faces ; and by the *angles*, the angles formed by the incidence of the faces.

If all the faces on a given crystal be alike (*similar faces*), the crystal form is termed "*simple*," but if they be different (*dissimilar faces*), the crystal form is termed "*complex*" or "*compound*."

The "dominant," "fundamental," or "primary" form of a compound crystal is that form determined by the largest faces (dominant faces). The other faces are termed "subordinate" or "secondary" faces.

The *axes* of crystals are imaginary straight lines drawn from points or parts (angles, edges, or surfaces) on one side of a crystal to similar parts on the opposite side, and which lines would intersect at some central part of the crystal.

The classification of crystals is founded on the measurements and positions of the axis :—

I.—CUBIC OR REGULAR SYSTEM.

(1.) *Character.*—Three equal axes intersecting one another at right angles.

(2.) *Forms.*—Cube—regular octahedron—rhombic dodecahedron—tetrahedron.

(3.) *Examples.*—(*a*) *Elements :* Most of the metals—phosphorus.
(*b*) *Compounds :* Most chlorides, bromides, iodides, fluorides and sulphides—magnetic iron ore—the alums—lead nitrate.

II.—Quadratic or Square Prismatic System.

(1.) *Characters.*—Three axes intersecting one another at right angles, two being of equal length, and the third (the principal axis), either longer or shorter than the other two.

(2.) *Forms.*—Square prism — square or quadratic octahedron—double four-sided pyramid with square base.

3.) *Examples.*—(*a*) *Elements :* Palladium.
(*b*) *Compounds :* Mercurous chloride—potassic ferrocyanide—stannic oxide—copper pyrites—oxalate of lime.

III.—Rhombohedric or Hexagonal System.

(1.) *Characters.*—Four axes—three being equal and in one plane, intersecting one another at angles of 60°. The fourth axis (the principal axis) is longer or shorter than the other three, and is situate at right angles to the plane occupied by them.

(2.) *Forms.*—Rhombohedron — double six-sided pyramid—scalene and isosceles dodecahedra.

(3.) *Examples.*—(*a*) *Elements :* Tin—antimony—arsenicum—thallium—plumbago.
(*b*) *Compounds :* Snow—cinnabar—magnetic pyrites—carbonates of lime—magnesia—zinc—quartz, beryl—sodic nitrate.

IV.—Rhombic or Right Prismatic System.

(1.) *Characters.*—Three axes of unequal length, intersecting one another at right angles.

(2.) *Forms.*—Right rectangular and right rhombic prisms and octahedra.

(3.) *Examples.*—(*a*) *Elements:* Iodine—native sulphur (or sulphur crystallized from solutions)—selenium.
(*b*) *Compounds :* Manganese peroxide—baric and mercuric chloride—orpiment—antimonic oxide—carbonates of lead—barium, strontium, potassium and ammonium—arragonite—nitrates of silver, potassium, and ammonium—sulphates of magnesium, zinc, barium, and strontium—tartar emetic—Rochelle salt—citric acid—morphia.

V.—Monoclinic or Oblique Prismatic System.

(1.) *Characters.*—Three unequal axes, two of which intersect obliquely, whilst the third (principal axis) is placed perpendicularly to their plane.

(2.) *Forms.*—Oblique rectangular and oblique rhombic prisms and octahedra.

(3.) *Examples.*—(*a*) *Elements:* Sulphur.
(*b*) *Compounds:* Sulphides of arsenic (red) and antimony—carbonates of soda and potash—sulphates of soda, lime, and iron—chlorate of potash—borate and phosphate of soda—chromate of lead—acetates of soda, copper, zinc, and lead—tartaric and oxalic acids.

VI.—THE TRICLINIC OR DOUBLE OBLIQUE SYSTEM.

(1.) *Characters.*—Three unequal axes intersecting obliquely.
(2.) *Forms.*—Doubly oblique prisms and octahedra.
(3.) *Examples.*—(*a*) *Elements:* None.
(*b*) *Compounds:* Boric acid—sulphate of copper—nitrate of bismuth—gallic acid.

We shall consider in Section I. *the non-metals* (metalloids), commencing with oxygen. In each case the compounds the body forms with those elements already considered, will be examined in detail. Each element and compound will be examined as far as practicable in the following order: (1) Synonyms; (2) History; (3) Natural History; (4) Preparation; (5) Properties—(α) sensible, (β) physical, (γ) chemical, (δ) physiological; (6) Tests; (7) Uses in Nature, Arts, and Medicine.

In Section II. we shall consider *the metals*, their compounds amongst themselves (alloys and amalgams) and their compounds with the non-metals (salts).

Adopting this division of the elements for convenience, it must be remembered that it (like all classifications) is purely arbitrary. Thus arsenic has by some been placed amongst the non-metals, and hydrogen (on account of its chemical behaviour) amongst the metals.

Section III. will be devoted to *Organic Chemistry.*

We shall examine the non-metals in the following order:—

	Symbol.	Atomic Weight.	Relative Weight. H = 1		Symbol.	Atomic Weight.	Relative Weight.
Oxygen	O.	16	16	Sulphur ..	S.	32	32
Fluorine....	F.	19	19	Selenium ..	Se.	79	79
Chlorine....	Cl.	35·5	35·5	Tellurium..	Te.	125	125
Bromine....	Br.	80	80	Carbon	C.	12	
Iodine	I.	127	127	Boron	B.	11	
Nitrogen ..	N.	14	14	Silicon	Si.	28	
Phosphorus .	P.	31	62	Hydrogen ..	H.	1	1

SECTION I.—THE NON-METALS.

CHAPTER IV.

OXYGEN.

OXYGEN: — Synonyms — History — Natural History — Preparation — Properties. OZONE; History—Natural History—Preparation—Properties—Tests—Quantitative Determination—Uses of Oxygen—Respiration—Combustion.

OXYGEN (O'').

Atomic weight = 16 [*more accurately* 15·96]. *Molecular weight* = 32. *Dyad''* (H_2O—Ag_2O). *Molecular volume* $\boxed{\ \ |\ \ }$. *Specific gravity observed* 1·1056; *theoretic* (0·0693 × 16) 1·1088. 1 *litre weighs* 16 *criths* (0·0896 *grm.* × 16) = 1·4336 *grm. at* 0° *C. and* 760 *millimètres*; 100 *cubic inches weigh* 34·288 *grains at* 60° *F. and* 30 *B. P.*

Synonyms: *Spiritus Nitro-aërius* (Mayow, 1674); *Dephlogisticated air* (Priestley, 1774); *Empyreal air* (Scheele, 1775); *Pure air* (Lavoisier, 1777); *Vital Air* (Condercet, 1777); *Oxygen* (Lavoisier, 1778), (from ὀξὺς acid, and γεννάω, I generate).

History (*a*).—The earlier investigators devoted much attention to the nature of what they termed "*a calx*," that is the residue left after the body had been exposed to fire. *Ray*, in 1630, thought that a calx resulted from the fixation of air; *Boyle*, in 1660, regarded it as due to the fixation of heat; *Hooke*, in 1670, again insisted that it was to be explained by fixation of air; whilst *Mayow*, in 1674, said it depended on the fixation of some substance similar to that existing in saltpetre, and which he termed "the nitro-aërial spirit." Thus in great measure, Mayow anticipated Lavoisier's discoveries respecting combustion. His views were not, however, accepted, being opposed to the then dominating theories of Beccher and Stahl.

(*b*) *Experimental facts.*—Priestley, on August 1, 1774, whilst heating "red precipitate," or the calx of mercury as it was called (HgO) in a glass bulb over mercury obtained a gas (oxygen), which he named, in accordance with the Stahlian theory "Dephlogisticated air."

In 1775, Scheele (of Upsala, in Sweden), whilst examining the action of sulphuric acid on peroxide of manganese (pyrolusite) obtained a gas (oxygen) which he called "empyreal air," because of the energy with which it supported combustion.

Lavoisier (unfairly no doubt) claimed its discovery. He, however, was the first to explain the true nature of "red precipitate" from which Priestley, in the first instance, had prepared it, and showed that the process was merely an indirect means of obtaining oxygen from the air. Further, Lavoisier disputed the truth of the Stahlian theory (which taught that when any substance was burnt, it *gave out* "phlogiston"), proving by actual experiment that the product of the combustion of phosphorus (*i.e.*, P_2O_5, or the calx) was heavier than the original phosphorus, and that therefore phosphorus could not have *given out* anything in burning, but must have *taken in* something. The Stahlians, to meet this difficulty (which, however, can scarcely be regarded as originating with Lavoisier, seeing that it was the subject of experiment many years previously by Le Brun and Jean Ray), imbued phlogiston with the property of levity. Lavoisier, soon after this, propounded a new theory of combustion, which was destined to overthrow the phlogistic theory. This was, "that combustion was the combination of a burning body with oxygen." He moreover rejected Priestley's name, "dephlogisticated air," and called the newly-discovered gas oxygen, or acid-begetter (ὀξὺς and γεννάω), believing it not only to enter into the composition of all acids, but to constitute the acidifying principle.

Natural History.—Oxygen is the most abundant and widely-diffused element in nature. Excepting in atmospheric air, however, it is always found combined:—

(*a.*) *The Mineral Kingdom.*—(1.) The *solid crust* of the *earth* consists of three chief constituents—viz., *carbonate of lime* ($CaCO_3$), of which $\frac{48}{100}$ is oxygen; *clay* (Al_2O_3), of which $\frac{48}{102}$ is oxygen; and *silica* (SiO_2), of which $\frac{32}{60}$ is oxygen. Thus about one-half of the *solid crust* of the earth is oxygen; (2) whilst of the *water*, or liquid part, $\frac{8}{9}$ by weight is oxygen, and (3) of the *air* or gaseous portion, $\frac{1}{5}$ by volume or $\frac{2}{9}$ by weight is oxygen.

(*β.*) *The Vegetable Kingdom.*—About one-fourth part of all growing vegetable matter is water, $\frac{8}{9}$ of which is oxygen; whilst of the solid part, which is principally cellulin ($C_6H_{10}O_5$) about $\frac{1}{2}$ is oxygen.

(*γ.*) *The Animal Kingdom.*—Water constitutes about 75 per cent. of living animals, $\frac{8}{9}$ of which is oxygen. Of albuminous matters, nearly $\frac{1}{4}$ is oxygen.

Preparation.—Although present so largely in air, the nitrogen, with which the oxygen is mechanically mixed, cannot be directly separated. For oxygen is singularly energetic, and nitrogen singularly inert, in chemical relationship. Thus to prepare oxygen from the air, indirect processes have to be adopted.

These are as follows:—

(A.) *By the action of heat on certain metallic oxides and peroxides*:—

(1.) *Mercuric oxide* (HgO); Priestley, 1774; (216 grains produce 16 grains of oxygen).

$$2HgO = 2Hg + O_2.$$
Mercuric oxide = Mercury + Oxygen.

(2.) *Red lead* (Pb_3O_4; triplumbic tetroxide); Priestley, 1774; (655 grains produce 16 grains of oxygen)—

$$2Pb_3O_4 = 6PbO + O_2.$$
Triplumbic tetroxide = Plumbic oxide (*Litharge*) + Oxygen.

(3.) *Manganese dioxide* (Pyrolusite, Black oxide of Manganese); Scheele, 1775; (261 grains produce 32 grains of oxygen = 93·4 inches)—

$$3MnO_2 = Mn_3O_4 + O_2.$$
Manganese dioxide = Trimanganic tetroxide + Oxygen.

(4.) *Baric peroxide*; Boussingault, 1851; (*Ann. Chim. Phys.*(3)xxxv.) Brin Frères,* 1885); (169 grains produce 16 grains of oxygen)—

[Note. At 1022° F. (550° C.), BaO becomes BaO_2, but at 1472° F. (800° C.) BaO_2 is decomposed as follows:—]

$$2BaO_2 = 2BaO + O_2.$$
Baric peroxide = Baric oxide + Oxygen.

(5.) *Auric, argentic, platinic, and chromic* (CrO_3) *oxides*, etc., lose all or a portion of their oxygen when heated.

(B.) *By the action of heat on certain salts rich in oxygen*—such as the perchlorates, chlorates, chlorites and hypochlorites, the perbromates and bromates, the periodates and iodates, the nitrates and nitrites, &c.

(1.) *Potassic chlorate* (Gay Lussac, 1814); (122·6 grains yield 48 grains of oxygen). To effect decomposition, a temperature is required above the fusing point of the salt [*i.e.*, about 662° F. (350° C.)].

The reaction occurs in two stages:—

(*α*.) A potassic perchlorate is first formed—

$$2KClO_3 = KCl + KClO_4 + O_2.$$
Potassic chlorate = Potassic chloride + Potassic perchlorate + Oxygen.

(*β*.) The potassic perchlorate is then decomposed—

$$KClO_4 = KCl + 2O_2.$$
Potassic perchlorate = Potassic chloride + Oxygen.

Stating the reaction in a single equation, we may express the decomposition thus:—

$$2KClO_3 = 2KCl + 3O_2.$$

(2.) When potassic chlorate is mixed with manganese dioxide or with certain other oxides (as ferric oxide), or with spongy platinum, it evolves oxygen at a temperature considerably below the fusing point of the salt (about 392° F. or 200° C.), in other words at about 270 degrees F. (150 degrees C.) below that at which it is generated without the manganese oxide. According to the experiments of Wiederhold (*Pogg. Ann.* cxvi., p. 171), confirmed by Baudrimont (*J. Pharmacie*, S. IV., xiv., pp. 81 and 161) no perchlorate is formed under these conditions.

---

* The Brothers Brin, of Paris, have suggested this as a commercial method for obtaining an unlimited supply of oxygen.

[To free the gas from traces of chlorine likely to be generated when thus prepared, it should be passed through a wash-bottle containing caustic soda. Further, if the oxide of manganese contains carbon as an impurity, an explosion may occur when the oxygen mixture is heated, or traces of CO_2 will be generated, which will also be absorbed by the caustic soda solution.]

The explanation of this action of the manganese dioxide is not well understood. The oxygen obtained, it is certain, is evolved primarily from the chlorate and not from the oxide; but the manganese oxide may undergo a higher oxidation at a temperature below that at which the potassic chlorate could yield free oxygen, these higher oxides readily parting with the oxygen thus combined, again returning to the condition of the lower oxide. (See page 13. See also p. 72 for a possibly analogous action in the case of cobaltic oxide.)

(3.) *Zincic sulphate;* (Deville and Debray) (161 grains produce 16 grains of oxygen)—

$$2ZnSO_4 = 2ZnO + 2SO_2 + O_2.$$

Zincic Sulphate = Zincic oxide + Sulphurous anhydride + Oxygen.

(4.) *Alkaline nitrates;* (101 grains of KNO_3 produce 32 grains of oxygen).

(5.) *Permanganates with superheated steam* (Marechal and Tessié du Mothay); (316·2 grains of steam and K_2MnO_4 produce 64 grains of oxygen)—

$$4K_2MnO_4 + 4H_2O = 8KHO + 2Mn_2O_3 + 3O_2.$$

Potassic permanganate + Steam = Potassic hydrate + Dimanganic trioxide + Oxygen.

If a current of air be passed over the red hot residue, the permanganate will be reproduced. Thus the same permanganate may be used over and over again.

(C.) *By heating certain compounds rich in oxygen with sulphuric acid.*

(1.) *Manganese dioxide and sulphuric acid;* (87 grains of MnO_2 produce 16 grains of oxygen)—

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

Manganese dioxide + Sulphuric acid = Manganous sulphate + Water + Oxygen.

(2.) *Potassic bichromate and sulphuric acid* (295 grains of potassic bichromate produce 48 grains of oxygen).

The reaction may be stated as occurring in two stages as follows:—

(*a*). $K_2Cr_2O_7 + 2H_2SO_4 = 2KHSO_4 + 2CrO_3 + H_2O.$

Potassic bichromate + Sulphuric acid = Potassic hydric sulphate + Chromic oxide + Water.

(*b*.) $4CrO_3 + 6H_2SO_4 = 2Cr_2(SO_4)_3 + 6H_2O + 3O_2$.
Chromic oxide + Sulphuric acid = Chromic sulphate + Water + Oxygen.

Or, written in a single formula, it may be stated as follows:—

$2K_2Cr_2O_7 + 8H_2SO_4 = 2KHSO_4 + 2Cr_23SO_4 + 8H_2O + 3O_2$.
Potassic bichromate + Sulphuric acid = Potassic sulphate + Chromic sulphate + Water + Oxygen.

(3.) *Plumbic peroxide and sulphuric acid* (239 grains of plumbic peroxide produce 16 grains of oxygen)—

$2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O + O_2$.
Plumbic peroxide + Sulphuric acid = Plumbic sulphate + Water + Oxygen.

(D.) *By the action of various oxides on hydric peroxide*:—

$H_2O_2 + Ag_2O = H_2O + Ag_2 + O_2$.
Hydric peroxide + Argentic oxide = Water + Silver + Oxygen.

(E.) *By the electrolysis of acidulated water*, the oxygen being evolved at the positive pole.

(F.) *By passing a mixture of steam and chlorine through a red hot porcelain tube*:—

$2H_2O + 2Cl_2 = 4HCl + O_2$.
Water + Chlorine = Hydrochloric acid + Oxygen.

(G.) *By heating to 176° F. (80° C.) a solution of bleaching powder with a small quantity of cobalt oxide or chloride, or by passing chlorine through a hot solution of sodic or potassic hydrate, containing a little chloride or nitrate of cobalt.* The chlorine converts the cobaltous hydrate into cobaltic hydrate, and subsequently the liquid effervesces and evolves oxygen. (Mitscherlich, 1843; Fleitmann, 1865.)

The reactions may be stated in two stages as follows:—

(*a*.) $CaCl_2O_2 + 4CoO = CaCl_2 + 2Co_2O_3$.
Bleaching powder (Solution calcium hypochlorite) + Cobaltous oxide = Calcium chloride + Cobaltic oxide.

(*b*.) $2Co_2O_3 = 4CoO + O_2$
Cobaltic oxide = Cobaltous oxide + Oxygen.

Thus all the oxygen of the bleaching powder is evolved.

(H.) *By dropping sulphuric acid into a red-hot platinum retort or upon broken bricks heated to redness.* (Deville and Debray.) By this means the acid yields about 15·6 per cent. of its weight of the gas. Every 1000 grains of acid will yield in practice about one-fourth of a cubic foot of gas.

$2H_2SO_4 = 2H_2O + 2SO_2 + O_2$.
Sulphuric acid = Water + Sulphurous anhydride + Oxygen.

[The SO_2 is absorbed by passing it through a coke scrubber wetted with water. The sulphurous acid solution may be utilised in the leaden chamber for the preparation of fresh sulphuric acid.]

(I.) *By the action of the leaves of plants in sun-light on carbonic acid*, whereby the carbon is fixed, and oxygen is set free.

Properties.—(α.) *Sensible.*—A colourless, inodorous, tasteless gas.

(β.) *Physiological.*—If a rabbit be placed in pure oxygen at 75° F. (24° C.), it lives for about three weeks, eating voraciously all the time, but nevertheless becoming thin. The action of oxygen at 45° F. (7·2° C.), is to produce narcotism, and eventually death. When oxygen is cooled by a freezing mixture, it induces so intense a narcotism that operations may be performed under its influence.

Compressed oxygen is "the most fearful poison known." The pure gas at a pressure of 3·5 atmospheres, or air at a pressure of 22 atmospheres, produces violent convulsions, simulating those of strychnia poisoning, ultimately causing death. The arterial blood in these cases is found to contain about twice the quantity of its normal oxygen. Further, compressed oxygen stops fermentation, and permanently destroys the power of yeast. (Paul Bert.)

(γ.) *Physical.*—Oxygen is 16 times heavier than hydrogen. Its experimental specific gravity is 1·1056 (Air = 1), so that 100 cubic inches weigh 34·288 grains. Its relative weight is 15·96 (hydrogen = 1). A litre at 0° C. and 760 mm. weighs 1·43 grms. Until lately oxygen was regarded as a permanent gas. Under a pressure of 300 atmospheres, and a cold of —110° C., Pictet condensed it into a transparent liquid having a specific gravity of 0·978 at —166° F. (—130° C.), Wroblewski and Olzewski abroad, and Dewar in this country, have liquefied it under a pressure of 22·5 atmospheres at —136° C, employing for this purpose the cold produced by the boiling of liquid ethylene. Oxygen refracts light less powerfully than any other gas (O = 0·8, air = 1). It is evolved from the positive pole of the battery (electro-negative). It is the only gas which is magnetic, its magnetism being feeble, diminished by heat and increased by cold. Heat (as in the case of all other gases) expands the gas 0·003665 times its volume for every 1° C., or 0·002 times its volume for every 1° F. It is only slightly soluble in water; 100 volumes of water at 0° C. absorb 4·114 volumes, and 2·9 volumes at 15° C. measured at normal pressure and temperature. At higher temperatures the solubility decreases. 100 volumes of absolute alcohol dissolve about 28 volumes of the gas. It is rapidly absorbed both by solutions of potassic pyrogallate or of sodic dithionite in water.

(δ.) *Chemical.*—Oxygen is without action either on litmus or on turmeric. It causes no precipitate with lime water. With nitric oxide (N_2O_2) it forms red fumes of N_2O_4. It is completely absorbed by a solution of pyrogallic acid in strong caustic potash. It supports combustion vigorously, but is not itself combustible ;—hence Lavoisier's theory of combustion, that it was "*rapid oxidation.*"

Action on the non-metals.—Oxygen combines with all the non-metals, except with fluorine. Further, it combines with them *directly*, except with chlorine, bromine, and iodine, with which elements combination is indirect only, that is, through the intervention of a third body. It combines, however, with none of the non-metals *at ordinary temperatures*, except with phosphorus, in which case the energy of oxidation may be so intense as to effect combustion. If carbon, sulphur, or phosphorus be burnt in oxygen, bodies are formed (viz., CO_2, SO_2, and P_2O_5), which, when dissolved in water, redden litmus. All the non-metals, except hydrogen and fluorine, form, by their union with oxygen, anhydrides—that is, bodies which form acids when dissolved in water. Hence, Lavoisier taught "that oxygen was the acidifying principle of all acids," a theory we now know to be incorrect.

Action on the metals.—There are certain metals which in a molten state absorb oxygen, evolving it again on cooling. Of these silver is a notable illustration. When molten it absorbs ten times its bulk of the gas, its evolution on cooling effecting what is termed "spitting," *i.e.*, the surface of the silver becoming uneven from volcanic-like projections. Oxygen combines directly, under certain conditions, with all the metals, except with gold, silver, and platinum (noble metals), where combination can only be effected indirectly. Again, combination does not take place at ordinary temperatures, except with a few metals, such as sodium, potassium, barium, strontium, and calcium, and in certain cases where the metals have been reduced to a state of minute subdivision (pyrophoric). Only a very moderate heat, however, is usually required to effect union. Iron, lead, etc., undergo superficial oxidation in the air at common temperatures, but this is dependent on the existence of conditions that favour oxidation, such as the presence of moisture, carbonic anhydride, etc.

When a metal combines with oxygen, it generally forms what is called a *base*, that is, "*a compound body capable, completely or in part, of neutralizing an acid.*" The compounds, formed by the union of the alkaline metals with oxygen, are called alkalies or alkaline bases, such as *e.g.*, sodic oxide (Na_2O) potassic oxide (K_2O), etc. These bodies are very soluble in water. The other metals also form bases with oxygen, but they are practically insoluble in water ; nevertheless they are capable either entirely or in part of neutralizing acids (ZnO—Fe_2O_3). No non-metal ever forms a base by its union with oxygen, but some metals form anhydrides by such combination. This metallic anhydride is always the highest oxide that the metal is capable of forming, as *e.g.*, stannic anhydride, SnO_2—antimonic anhydride, Sb_2O_5, etc. There are certain oxides that are neither acids nor bases, and are known as "*indifferent oxides*" from their similarity to salts. Such, for example, are water (H_2O), manganese dioxide (MnO_2), etc.

Various methods have been devised for estimating the quantity of free oxygen present in a mixed gas. In most cases the oxygen is removed by absorbent agents, such as moist phosphorus or certain moist metals (iron, lead, etc.) ; certain low oxides, such as FeO or N_2O_2 (Priestley) ; or a mixture of the last two bodies (Davy) ; the ammonio-chloride of copper (Graham) ; pyrogallic acid dissolved in an alkaline solution (Liebig) ; red-hot copper or iron (Dumas) ; cuprous oxide (Cu_2O) in ammonia (*Chemical News*, vol. xxxiii., p. 5) ; also by exploding the gas with hydrogen. These methods of estimating oxygen will be referred to under the analysis of air.

Ozone (ὄζω, I smell) : Allotropic or Active Oxygen.

Molecular weight = 48 (47·88). *Density* 23·94. *Molecular volume* ☐☐.

History.—*Von Marum* (1780) noticed that when electric sparks had been passed through air or oxygen, the gas possessed a peculiar odor, and rapidly tarnished quicksilver. Schönbein, of Basle, in 1840, showed that this peculiar smelling gas was developed by exposing moist phosphorus to air. Since 1840 ozone has been further examined by Marignac, De la Rive, Fremy, Becquerel, Odling, Andrews, &c.

Natural History (*See* OZONE under AIR).

Nature of Ozone.—Schönbein, in the first instance, regarded ozone as peroxide of hydrogen (H_2O_2 or in old formula HO_2) ; Baumert and Williamson independently fixed H_2O_3 as its composition, because water and oxygen, as they supposed, were formed by its decomposition : ($H_2O_3 = H_2O + O_2$). Berzelius, Marchand, Erdmann, Marignac, De la Rive, Fremy, Becquerel, and Andrews afterwards showed that pure *dry* oxygen could be ozonized, whilst Andrews proved that with proper precautions no water results from its decomposition. Schönbein afterwards regarded ozone as permanently negative oxygen ($\overset{-}{O}$), there being as he thought, a permanently positive oxygen ($\overset{+}{O}$) (antozone) (see page 80).

Chemists are now agreed that ozone is an allotropic oxygen, where three volumes are condensed into two. This view, first reasoned out by Odling, was afterwards confirmed by the observations of Andrews, who showed that (1) ozonization is accompanied by a gradual diminution in the bulk of the gas ; (2) that when the ozonized oxygen is heated, it returns to its original bulk, and (3) that when ozone is absorbed by mercury or by potassic iodide, the volume of the gas is not affected. (*Phil. Trans.*, 1860, p. 113.) Thus :—

$$\underbrace{OOO}_{\text{2 vols. of Ozone.}} + Hg = HgO + \underbrace{OO}_{\text{2 vols. of common O.}}$$

Further confirmation of this view was obtained by Soret, who found that the increased volume of an ozonized oxygen when decomposed by heat was one-half the decrease of volume when the same ozonized oxygen was treated with bodies like oil of thyme, which absorb it without decomposing it. Brodie and Soret have verified the same fact by observing rapidity of diffusion, diffusion being known to occur inversely as the square root of the density. (*See* DIFFUSION.) Soret showed that 271 volumes of ozone diffused in the same time as 227 volumes of chlorine, or as 1 volume of ozone to 0·8376 volume of chlorine, a relationship closely expressed by the theoretical statement

$$\sqrt{35{\cdot}5} : \sqrt{24{\cdot}0}.$$

Preparation.—Ozone, however prepared, always contains a large admixture of air or oxygen. Hence our knowledge of it relates to a dilute body. The following are some of the methods by which a mixture of ozone (say, at most, a 20 per cent. mixture) with air or oxygen may be obtained.

(1.) By *electrical agency.* The silent passage of electricity through damp oxygen, is the method best adapted for its generation. A small induction spark, or the brush from the electrical machine, may also be employed, but the long spark from the coil, on account of its high temperature, destroys the ozone as fast as it is generated. Various ozonizers have been invented, in order to secure this silent passage of electricity through oxygen. That of *Houzeau* consists of a glass tube filled with oxygen, a platinum wire being placed in the centre of the tube, and attached to one terminal of an induction coil, whilst a second wire is wound round the glass tube and attached to the other terminal. *Siemen's ozonizer* consists of two glass tubes, one placed inside, but separated by a small interval from the other, through which interspace a stream of oxygen may be continuously passed. The internal tube has its inner surface, and the external tube its outer surface, covered with tin-foil. When these are connected with different poles of the coil, a silent discharge takes place between them, whereby the ozonization of the intermediate oxygen is effected. By means of these ozonizers, 60 to 120 milligrammes of ozone per litre of oxygen may be obtained.

It is most important in the preparation of ozone to keep the temperature low by the use of freezing mixtures.

(2.) By the *electrolysis of dilute sulphuric acid.* The oxygen set free at the positive pole by the electrolysis of dilute sulphuric acid contains about $\frac{1}{250}$ part of its volume of ozone, *i.e.*, about 3 to 5 milligrammes per litre.

When perfectly dried the odour of the electrolytic oxygen remains, whilst if it be subjected to heat, the smell, as well as the active oxidizing power, of the gas is destroyed without any trace of moisture being produced, thereby proving that electrolytic oxygen is not, as was once supposed, an oxide of hydrogen.

The water mixed with the acid should be free from all organic or other oxidizable matters, and the presence of a little bichromate of potash in solution is said to assist its formation. (Baumert.)

(3.) By *slow combustion* (Eremacausis) : (*a*) *of phosphorus in moist air* (Schönbein.) The phosphorus employed should be freshly scraped, and kept at a temperature of from 70° to 90° F. (21° to 32° C.). It should not be allowed to act on the same air for more than an hour, otherwise the ozone first generated will be decomposed. The action is more complete if the air in the vessel be slightly rarefied, the best effects being produced by employing a mixture of hydrogen and oxygen in the place of air. The gas must afterwards be washed with water to free it from phosphorous acid. (*β.*) By the *slow combustion of ether and volatile oils.* When the combustion of ether is effected by glowing platinum, or by placing a hot glass rod in a bottle filled with the vapor, ozone is produced, together with certain acid vapours. Aromatic plants and flowers are also said to generate ozone (Mantegazza).

(4.) By the *rapid combustion of all bodies containing hydrogen.* The generation of ozone under these conditions is supposed to be due to the hydrogen molecule combining with a half-molecule of oxygen (*a*), leaving the other oxygen atom free to combine with a second oxygen molecule to form ozone (*β*). Thus—

$$(a.)\ H_2 + O_2 = H_2O + O\ ;\quad (\beta.)\ O + O_2 = O_3.$$

Ozone is not formed by the combustion of carbon, inasmuch as carbon combines not with half-molecules of oxygen (O), but with complete molecules (O_2). (Thau.)

(5.) By the *action of oxygen on fine particles and on large surfaces.* When lead pyrophorus is exposed to the air, it catches fire spontaneously owing to the generation of ozone by the action of air on the finely-divided metallic particles.* Similarly, when phosphorus is dissolved in bisulphide of carbon, and the solvent allowed to evaporate, the finely-divided phosphorus fires spontaneously.

(6.) By *nascent action.* The intense activity of nascent oxygen, it is thought, may be due to the gas being ozonic. Probably the oxygen set free by plants from the decomposition of carbonic anhydride is also ozonic. (De Lucca, *Pharmaceutical Journal,* July, 1873, p. 65.) Possibly to this may be traced the bleaching action of morning dew.

(7.) Ozone is also formed during the evaporation of water. (*Ann. Chem. Pharm.*, clxi., 232.) This, no doubt, explains the operation of meadow bleaching where damp linen is exposed to the air for the purpose of rendering it white. It also explains the occurrence of ozone in the neighbourhood of the sea.

---

* Possibly this action may be due to the carbon present absorbing oxygen, and so bringing it within the sphere of affinity.

Properties of Ozone.—(*α.*) *Sensible.*—A colorless, or probably blue-tinted gas, having a peculiar phosphorus-like odor (ὄζω, I smell). Pure ozone, that is, ozone free from air or oxygen, has never been prepared.

(*β.*) *Physiological.*—Its special action in respiration will be discussed further on (page 81). It acts as an intense irritant to the eyes and nose, and rapidly proves fatal to animal life. (Thénard, Schönbein, McKendrick and Dewar.)

(*γ.*) *Physical.*—At a temperature of —76°F.(—105° C.) (produced by the evaporation of liquid ethylene) and at a pressure of 125 atmospheres, ozone may be condensed into an indigo-blue liquid. The gas consists of 3 volumes of oxygen condensed into 2 volumes; hence its density must be $1\frac{1}{2}$ times that of common oxygen, and 1 litre must weigh (8×3) 24 criths (see page 34). It decomposes slowly in the presence of moisture at 212° F. (100° C.). If kept in dry and sealed tubes, it may be preserved for a long time, although it ultimately decomposes. Decomposition is instantaneous at a temperature of from 450° to 500° F. (232° C. to 260° C.), the ozone becoming ordinary oxygen with a corresponding increase of bulk. It is decomposed when agitated with finely-powdered fragments of glass. Ozone is slightly soluble in water, the solution having the smell peculiar to the gas. At 32° F. (0° C.) 100 volumes of water dissolve $\frac{1}{2}$ volume of ozone (Carius). It is far more soluble in certain ethereal oils and in bisulphide of carbon, its solution in the latter forming a blue liquid. It is not soluble in solutions of acids or alkalies.

(*δ.*) *Chemical.*—Ozone is a powerful oxidizer. This action depends on its desire to throw off one of its oxygen atoms, and so return to the condition of ordinary oxygen. It bleaches litmus, and is as powerful a supporter of combustion as ordinary oxygen. 29,600 units of heat are absorbed in the formation of ozone from oxygen. Hence its greater chemical activity, this heat being liberated when oxidation is effected through its agency.

(1.) *Action on the non-metallic elements.*—These are as a whole but little, and but slowly, affected by it. It rapidly oxidizes the compounds of hydrogen with phosphorus, sulphur, and selenium. There is some doubt whether or not it can effect the conversion of nitrogen into nitric acid in the presence of water.

(2.) *Action on metals.*—None of the metals, except mercury, are affected by dry ozone, whilst in the presence of moisture nearly all the metals (except gold and platinum) are oxidized by it. Even metallic silver is converted into a peroxide. It is to be noted that, under these circumstances, no contraction of the gas results, the ozone returning from the triatomic to the diatomic condition of ordinary oxygen.

Its action on mercury is remarkable. The mobility of the metal is at once destroyed, and the mercury rendered adherent, when shaken, to the glass vessel in which it is contained.

(3.) *Action on mineral compounds.*—Ozone converts the protoxides and protosalts of lead, tin, iron, manganese, etc., into peroxides and persalts. Some peroxides decompose ozone, and are themselves at the same time partially reduced. Thus the peroxides of copper, manganese and barium, etc., exhibit this catalytic action on ozone :—

$$BaO_2 + O_3 = BaO + 2O_2.$$

The sulphides and selenides are also oxidized by it into sulphates and selenates. Thus, black lead sulphide becomes a white lead sulphate, and ferrocyanides are converted into ferricyanides. It decomposes iodide of potassium, iodine being set free.

(4.) *Action on organic matter and on organic compounds.*—Organic bodies generally are speedily oxidised by ozone. It bleaches indigo (converting it into *isatin*), decolorizes blood, and converts alcohol into aldehyd. Tincture of guaiacum is turned green, and cork and caoutchouc are speedily acted upon by it. Putrid flesh is deodorized and albumen is destroyed by it. Strychnia and aniline assume various tints under its action. It is absorbed by turpentine, by oil of thyme, and by many essential oils without suffering decomposition. This circumstance has been employed by Soret to prove its composition, seeing that the diminution in volume occurring when ozonized oxygen is acted on by these absorbents, is exactly twice as great as the volume increase found after the ozone has been decomposed by heat. It has no action on paraffin, which may, therefore, be used for joining apparatus used in its generation, and in experiments upon it.

Ozone is used for bleaching discolored engravings.

Special Tests for Ozone.—(1.) White bibulous paper soaked in a solution of 1 part of potassic iodide, and 5 parts of starch, in 100 parts of water, constitutes the common ozone test-paper. Ozone, like chlorine and most oxidizing agents, displaces the iodine from its combination, the iodine thus set free blueing the starch :—

$$O_3 + 2KI + H_2O = 2KHO + I_2 + O_2.$$

For determining the presence of ozone in the air, Schönbein employed *moist* ozone papers, whilst Moffatt preferred them *dry*. For determining quantity the tint-depth is relied upon. The fallacies to the use of the iodide paper as a test for ozone, are the presence in the air of chlorine and of the oxides of nitrogen, these latter being formed in the air, as well as ozone, by electrical discharges.

(2.) *Houzeau's Ozonometer* consists of neutral litmus paper, soaked in a dilute solution of potassic iodide, the potash set free by the ozone turning the paper blue. A piece of the litmus paper without iodide, is also exposed to the air at the same time, a comparison of the two papers indicating how far the action on the iodide paper may be due to ammonia in the air, and not to the action of ozone.

(3.) A solution of *sulphate of manganese* is turned brown by ozone, owing to the formation of the hydrated manganous peroxide.

(4.) A colorless solution of a *protosalt of thallium* is turned yellow by ozone, but not by the oxides of nitrogen ("Intellectual Observer," 1867, p. 399). Böttger has suggested the use of thallous oxide paper on this ground.

(5.) Paper stained black with plumbic sulphide becomes white from the formation of sulphate.

Quantitative Determination.—This is made either (1) by means of a weighed quantity of dry mercury, which rapidly absorbs ozone, or (2) by estimating the amount of iodine liberated in a solution of potassic iodide of known strength, a little hydrochloric acid being added to prevent the absorption of carbonic acid:—

$$O_3 + 2KI + H_2O = O_2 + I_2 + 2KHO.$$

Antozone.

Schönbein first, and afterwards Brodie, directed attention to the fact that oxygen appears to exist in certain compounds, not only in a state different from, but actually antagonistic to, ozone. Schönbein termed this form of oxygen, *antozone*. Brodie was of opinion that the difference between ozone and antozone depended on the oxygen in the two cases existing in different polar conditions, the polarity being determined by the body with which it was associated (Odling, p. 125).

For example; (*a*.) The nascent oxygen evolved from *peroxide of manganese* (MnO_2), or from *peroxide of lead* (PbO_2), or from *chromic acid* (H_2CrO_4), or from *manganic acid* ($HMnO_4$), was regarded as ozonic, for in a nascent state it was found to color strychnia and guaiacum; whereas—

(*β*.) The nascent oxygen evolved from the *peroxides of barium, strontium, calcium*, and *hydrogen*, on the contrary, neither coloured strychnia nor tincture of guaiacum. Further, the oxygen obtained from these bodies seemed in some respects to be antagonistic to the ozone obtained from the former series (*a*) combining with it to form common oxygen.

These facts suggested the notion that the oxygen present in these bodies respectively must exist in different polar or electrical states, the one possessing the power of neutralizing the other. Thus—

$$\begin{array}{ccccccccc} \overset{+\,-\,-}{MnOO} & + & \overset{+\,-\,+}{H_2OO} & = & \overset{+\,-}{MnO} & + & \overset{+\,-}{H_2O} & + & \overset{+\,-}{OO} \\ \text{Peroxide of} & + & \text{Peroxide of} & = & \text{Manganese} & + & \text{Water} & + & \text{Common} \\ \text{manganese} & & \text{hydrogen} & & \text{oxide} & & & & \text{oxygen.} \end{array}$$

Recent researches have, however, proved beyond doubt that this antozone is merely peroxide of hydrogen. (*See* Index.)

Uses of Oxygen. A. In Nature.—Oxygen acts as the great burner up of dead organic matter. We see *eremacausis* or slow oxidation taking place in the decay of wood (dry oxidation), in the formation of humus and peat (wet oxidation), and in the change of wood into coal (wet and imperfect oxidation). In *nitrification* we see the action of oxygen producing nitres. Oxygen effects the *resinification* of the fixed and volatile oils, illustrated in the drying of paint, in the occasional firing of greasy rags, and more generally in the formation of resins. The *acetification* of alcohol, again, is an oxidizing action: thus—

$$\underset{\text{Alcohol}}{C_2H_6O} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Acetic acid}}{C_2H_4O_2} + \underset{\text{Water.}}{H_2O}$$

B. In Respiration.—By the act of respiration the oxidation of tissue is effected. This process is common to all animals. Oxygen must be brought, by some means or other, into contact with the blood, and by it with the body generally. For this purpose we find in some animals a minute series of tubes, along which air is conveyed through the system. In fish, the water that contains oxygen in solution, passes through the gills, and coming into contact with a fine membrane, upon the opposite side of which the blood of the animal circulates, a free interchange of gases occurs. In some animals, as in frogs, respiration is, in great part (and in the higher animals in a lesser degree) cutaneous transpiration; whilst in animals generally the lungs constitute the principal machinery for effecting the proper oxygenation of the blood. In respiration the changes produced are threefold; (1) *a visible* or *color change;* (2) *a physical* or *heat change,* resulting from chemical combination; and (3) *a chemical change.* The facts of respiration were collected slowly; Mayow (1674) proved the taking in by the lungs of a something present in the air; Black (1757) proved the return of a something to the air during exhalation; whilst Lavoisier proved that the active gas taken in by the lungs was oxygen, and the gas returned carbonic anhydride. He was further of opinion that the animal heat was the result of a process of combustion, the union of carbon and oxygen. But he noted that the carbonic anhydride given back to the air, only accounted for a portion of the oxygen taken from the air.* Hence arose a theory of diffusion, which regarded respiration as a purely physical act. This may be stated as follows:—The venous blood, rich in carbonic acid but poor in oxygen, passes into the minute pulmonic capillaries, external to which is a mixed gas (the air), containing very little carbonic acid, but rich in oxygen; hence an interchange of gases takes place to establish equilibrium. More recent experiments, however, have shown that breathing is not merely a physical, but a chemical act. In the red blood-corpuscles a compound exists called "hæmoglobin." This body has a purple color in venous blood, but is capable of combining chemically with oxygen to form a vermilion red body called "oxy-hæmoglobin," the coloring matter of arterial blood. The active agent in respiration is this hæmoglobin, a body remarkable for the ease with which it both combines with, and delivers up oxygen. Asphyxia means the non-oxygenation of the purple hæmoglobin. Other gases, such as carbonic oxide, are also capable of combining with it, forming *e.g.* "*carbonic oxide hæmoglobin,*" which has a red color like oxy-hæmoglobin, but is unlike it, in that, when once formed, the hæmoglobin cannot part with the carbonic oxide, in the same way that it can with oxygen. Hence the cause of death in poisoning by this gas.

---

* Herbivorous animals are said to exhale carbonic acid in volume equal to the oxygen taken in, whilst carnivorous animals exhale a volume of carbonic acid 40 per cent. less than the inhaled oxygen.

Experiments (some teach) have shown that the blood corpuscles possess the power of ozonizing the oxygen inhaled, peroxide of hydrogen being formed by its combination with water. This compound is again decomposed into water and oxygen, which oxygen in its nascent state serves the purpose of oxidation. It is certain that both blood and hæmoglobin have the power of setting free the oxygen absorbed by oil of turpentine, and that blood globules act similarly on peroxide of hydrogen. The nascent oxygen thus evolved is capable of acting on such bodies as potassic iodide and starch, tincture of guaiacum, etc. In fact, Schönbein taught that the function of the blood corpuscles was the chemical excitement of the oxygen of the respired air. If hæmoglobin be mixed with alcohol or heated to 212° F., it then loses its power of decomposing the peroxide. Thus it is held that there is perpetually going on, in the animal organism, this formation and destruction of ozone and peroxide of hydrogen. The solution of the corpuscles, and their alteration into other products is believed to be due to the ozone. These products have no longer any plastic property, and in this way Schmidt believed the fluidity of the blood to be maintained. (Schönbein, Schmidt, Schreiber, etc.)

The quantity of oxygen required for respiration is important. It varies with sex, age, diet, exercise, etc. The following facts are important:—

I. *The Carbon daily consumed as food, and daily evolved as Carbonic Acid.* (Dr. E. Smith.)

Adult Man.	Carbon consumed in diet daily.		Carbon evolved by lungs daily as CO_2.	
	ozs.	grains.	ozs.	grains.
In idleness	8·72	3815	7·85	3434
With ordinary labor	13·00	5688	9·11	3985
With active work	15·60	6825	12·90	5644

The 3985 grains of carbon evolved per day from the lungs by a man in ordinary work is equivalent per hour to about 1240 cubic inches of carbonic acid.

Carbon consumed per hour by males (Andral and Gavarret).

Up to 8 years of age	77 grains.
From 8 to 15	133 ,,
,, 15 to 20	175 ,,
,, 20 to 40	185 ,,
,, 40 to 60	155 ,,
,, 60 and over	95 ,,

Females consume somewhat less, viz., 98 grains per hour from 15 to 40 years.

II. *The oxygen daily consumed by the food taken by an average man.* (The following results are the mean of the observations of Dumas, Liebig, Regnault, Lassaigne, Scharling, and Smith):—

	ozs.		cubic feet.
Oxygen consumed by the 9 ozs. of the carbon of food	24	=	17·73
,, ,, ,, ½ oz. ,, hydrogen ,,	4	=	2·95
Total of oxygen consumed daily	28	=	20·68

This is at the rate per hour of

1489 cubic inches of oxygen; or
7445 ,, ,, of air.

III. Normal air contains 0·04 per cent. (or 4 parts in 10,000) of carbonic acid. Air containing 4 per cent. of carbonic acid (the quantity present in air once breathed) is perfectly irrespirable; air containing 1 per cent. of carbonic acid is extremely distressing; air containing 0·1 per cent. may be regarded as polluted.

IV. It follows that the quantity of air used *per hour* (7445 cubic inches) *plus* that vitiated by the 1240 cubic inches of carbonic acid expired, must be—

At 4 per cent. of CO_2	38,445 cub. in.	= 22·22 cub. ft.
At 1 ,, ,,	131,445 ,,	= 76·08 ,,
At 0·1 ,, ,,	1,247,445 ,,	=723·64 ,,

V. The quantity of air required for respiration by an ordinary man is equal to that contained in a room 9 ft. square and 9 ft. high, renewed every hour, whilst for good breathing it should be renewed every half-hour. When, therefore, we fix 300 cubic feet as the space per head in sleeping-rooms, it is manifest that this must be regarded as a minimum, and implies thorough ventilation of the apartment.

VI. In these calculations the carbonic acid from the lungs is the only product considered. There is also, however, the carbonic acid given off from the skin, etc., which correctly should be taken into account.

It may be noted that a horse consumes about 13 times as much oxygen as a man ; that is, he requires about 19,000 cubic inches of oxygen, or 95,000 cubic inches of air, per hour.

C. As an Agent of Combustion.—The following table shows the quantity of oxygen consumed, the carbonic acid produced, and the air vitiated by the combustion of 1 lb. of the following substances—

One pound of	Cubic ft. of Oxygen consumed.	Cubic ft. of Air consumed.	Cubic ft. of Carbonic Acid (CO_2) produced.	Cubic ft. of Air vitiated (that is CO_2 = 1 per ct.)	Heat produced in lbs. of water raised 10°F.
Newcastle Coal	30·15	150·75	25·62	2713	1159
Dry Wood	15·85	79·25	15·30	1609	676
Dry Turf	17·15	85·75	16·51	1737	579
Coke	28·14	140·70	28·88	3129	1255
Charcoal	31·26	156·30	31·11	3267	1409
Camphine	38·90	194·5	27·8	2974·5	1957
Benzol	36·3	181·5	29·1	3091·5	1820
Spermaceti	37·0	185·0	25·2	2705·0	1759
Wax	37·7	188·5	25·6	2748·5	1581
Stearic Acid	34·6	173·0	24·0	2573·0	1705
Stearin	34·4	172·0	24·2	2592·0	1800
Paraffin	40·5	202·5	27·0	2902·5	2133
Paraffin Oil	40·5	202·5	27·0	2902·5	2133
Rape Oil	38·7	193·5	24·3	2623·5	1775
Sperm Oil	38·7	193·5	24·3	2623·5	1775
1 cubic foot of common coal gas = 14 candles	1·17	5·85	0·55	60·55	65
1 cubic foot of cannel coal gas = 20 candles	1·56	7·80	0·83	90·80	76

The following table shows the oxygen consumed, the carbonic acid produced, and the air vitiated, by the combustion of certain bodies, burnt so as to give the light of 12 standard sperm candles, each candle burning at the rate of 120 grains per hour each :—

Burnt to give light of 12 candles, each burning at the rate of 120 grains per hour.	Cubic ft. of Oxygen consumed.	Cubic ft. of Air consumed.	Cubic ft. of Carbonic Acid (CO_2) produced.	Cubic ft. of Air vitiated (that is CO_2 = 1 per ct.)	Heat produced in lbs. of water raised 10°F.
Cannel Gas	3·30	16·50	2·01	217·50	195·0
Common Gas	5·45	27·25	3·21	348·25	278·6
Sperm Oil	4·75	23·75	3·33	356·75	233·5
Benzole	4·46	22·30	3·54	376·30	232·6
Paraffin	6·81	34·05	4·50	484·05	361·9
Camphine	6·65	33·25	4·77	510·25	325·1
Sperm Candles	7·57	37·85	5·77	614·85	351·7
Wax ,, ...	8·41	42·05	5·90	632·25	383·1
Stearic ,, ...	8·82	44·10	6·25	669·10	374·7
Tallow ,, ...	12·00	60·00	8·73	933·00	505·4

It would thus appear that, of all the substances named, cannel gas vitiates air the least, and tallow candles the most, and that the order of their vitiating effect is also very nearly the order of their heating effect.

Regnault has shown that the same heat which will raise 1 lb. of water 1° F., will raise 49 cubic feet of air (= 3·6 lbs.) 1° F.; or, again, that the heat that will raise 1 cubic foot of water (= 62·23 lbs.) 1° F., will raise 3,054 cubic feet of air (= 233·71 lbs.) to the same extent.

D. As an Oxidizing Body.—Endless illustrations of this action might be given.

E. As a Medicinal Agent.—"Oxygenated water," and "peroxide of hydrogen," have been suggested and employed as medicinal agents, and particularly in oxaluria, a disease dependent on deficient oxidation. Their efficacy is more than doubtful.

Lastly, we note that the regular supply of oxygen in the air is maintained by plant-life, the carbon being retained in combination by the plant, whilst the free oxygen is evolved into the atmosphere for the support of animal life. Thus—

$$12CO_2 + 11H_2O = \underset{\text{Sugar.}}{C_{12}H_{22}O_{11}} + 12O_2.$$

CHAPTER V.

THE HALOGENS, OR HALOID ELEMENTS.

FLUORINE. CHLORINE: Compounds of Chlorine and Oxygen—Hypochlorous Anhydride—Hypochlorous Acid—Chlorous Acid—Chloric Peroxide—Chloric Acid—Perchloric Acid. BROMINE: Compounds of Bromine with Oxygen and Chlorine. IODINE: Compounds of Iodine and Oxygen—Iodic Acid—Periodic Acid—Compounds of Iodine and Chlorine—Generalization on the Halogens.

FLUORINE (F′).

Atomic weight, 19 [more accurately 19·1]. *Monad* (′) (*as in* HF) [also regarded by some as an octad]. *Specific gravity, theoretical* (0·0693 × 19) 1·3167. 1 *litre weighs* 19 *criths* (0·0896 × 19) = 1·7024 *grms., and* 100 *cubic inches weigh* 40·717 *grains, at* 60° *F. and* 30 *B.P.*

Synonyms.—*Fluoric Radical* (Berzelius); *Fluoricum; Fluorine* (Davy).

History.—That the fumes evolved by the action of heat on a mixture of sulphuric acid and fluor spar would etch glass was known in the 16th century. Scheele studied the composition of fluor spar. Gay Lussac and Thènard demonstrated that it was composed of calcium and hydrofluoric acid, which they, in common with Davy, believed to be an oxygen compound (fluate of lime). In 1812 and 1813, Davy obtained hydrogen at the negative pole and free fluorine at the positive pole by the electrolysis of hydrofluoric acid. Thus he demonstrated the analogy between hydrochloric and hydrofluoric acids, and also between chloride and fluoride of calcium. He was unable, however, to collect the fluorine, owing to its intense action on the vessels used in the experiment. As yet it has never (satisfactorily, at any rate) been isolated. The Messrs. Knox, of Dublin, in 1836, and Davy, in 1840, obtained fluorine by electrolysing hydrofluoric acid in fluor spar bottles. In 1858, Phipson is stated to have obtained it by heating together hydrofluoric and nitric acids. It has been examined at different times by Fremy, Baudrimont, Kammerer, and other chemists.

Natural History.—It is never found in nature in a free state. (*a.*) *In the mineral kingdom* it is tolerably abundant, as fluor or Derbyshire spar (CaF_2), and as cryolite ($6NaF,Al_2F_6$), a mineral found in

Greenland. It also exists as a fluoride of cerium, and is found in certain minerals, such as wavellite, mica, fluor, apatite, topaz, etc. It is present in sea and in many mineral waters. (β.) *In the vegetable kingdom* it occurs in numerous plants, and particularly in the siliceous stems of grasses. (γ.) *In the animal kingdom* it is found in the teeth, bones, milk, blood, urine, etc. Bone contains about 2 per cent. of fluoride of calcium (CaF_2).

Preparation.—It has never been isolated, because no vessel can be constructed to withstand its action. The methods attempted to effect its separation have been as follows :—

1. By the electrolysis of hydrofluoric acid in fluor spar vessels. (Davy and the Messrs. Knox.)

2. By the action of sulphuric acid on a mixture of dioxide of manganese and fluor spar :—

$$\underset{\text{Sulphuric acid}}{2H_2SO_4} + \underset{\text{Manganese dioxide}}{MnO_2} + \underset{\text{Calcic fluoride}}{CaF_2} = \underset{\text{Manganic sulphate}}{MnSO_4} + \underset{\text{Calcic sulphate}}{CaSO_4} + \underset{\text{Water}}{2H_2O} + \underset{\text{Fluorine}}{F_2}.$$

3. By electrolysing fused potassic fluoride. (Fremy.)

4. By heating to 170° F. (77° C.), a mixture of iodine with an excess of argentic fluoride for 24 hours in an hermetically sealed tube, in which the air has been previously displaced by iodine vapour, an iodide of silver and a fluoride of iodine (IF_5) being formed. (Kammerer.)

5. By the action of heat on cerium tetrafluoride. (Brauner.)

Properties.—(α.) *Sensible.*—A gas, said to have a yellow color, like chlorine. Its odor is very powerful.

(β.) *Physiological.*—Its action on the animal body is highly deleterious and irritating.

(γ.) *Physical.*—It has an estimated specific gravity of 1·3167; 100 cubic inches should weigh, therefore, 40·717 grains, and a litre 1·7024 grms.

(δ.) *Chemical.*—It combines with most of the elements, but not with carbon, nitrogen, sulphur, nor chlorine, and, strangely enough, not with oxygen. Its action on most bodies, especially on the metals (in which it even surpasses chlorine in activity), and on silicon, is intensely energetic. When allowed to act upon glass, the SiO_2 is converted into the volatile SiF_4. The difficulty of collecting the gas is so great that an accurate study of its properties is impossible. It is said to be absorbed by caustic potash, potassic fluoride and hydric peroxide being formed ($2KHO + F_2 = 2KF + H_2O_2$).

Later researches suggest that dry silver fluoride is not decomposed by chlorine, bromine or iodine at a red heat, whilst if a temperature above redness be employed, the liberated fluorine combines with the material of the containing vessel (carbon, platinum, gold or silver). (Gore "Phil. Trans.," 1870, p. 227.)

CHLORINE (Cl).

Atomic weight, 35·5 [more accurately 35·37]. *Molecular weight,* 71. *Molecular volume,* $\boxed{}\boxed{}$. *Atomicity monad* (′) (HCl) (regarded by some as an octad). *Specific gravity observed,* 2·47 ; *theoretic* (0·0693 × 35·37) 2·45012 ; 1 *litre weighs* 35·37 *criths* (0·0896 *grm.* × 35·5) = 3·1734 *grms.* 100 *cubic inches, at* 60° *F. and* 30 *B.P., weigh* 76·076 *grains.*

Synonyms.—*Dephlogisticated marine acid gas* (Scheele) ; *oxygenated muriatic acid gas* (Berthollet) ; *oxymuriatic acid* (Kirwan and Pearson) ; *muriaticum,* or *muriatic radical* (Berzelius) ; *Chlorine* (Davy, from χλωρὸς, green).

History.—Discovered by Scheele (1774) when acting on peroxide of manganese (pyrolusite) with hydrochloric acid. It was further examined by Berthollet (1785), and named by him "oxygenated muriatic acid gas," because, when placed in sunlight he found that the (moist) gas split up, as he supposed, into oxygen and muriatic acid. Gay Lussac and Thénard (1809) showed, however, that it was impossible to effect this decomposition with *dry* chlorine. Davy (1810) further proved its elementary nature.

Natural History.—It is never found free in nature. (*a.*) *In the mineral kingdom* it occurs in combination with sodium and other metals, in salt mines and in sea water, and in various horn-minerals such as lead, silver, mercury, etc. In volcanic districts it is found combined with hydrogen. (*β.*) *In the vegetable kingdom,* it is not an abundant element ; but in (*γ.*) *the animal kingdom,* it occurs in all secretions. Its absence from the urine in pneumonia, constitutes a peculiarity of that disease.

Preparation.—The first process described is the common laboratory process, and is that used in the B. P. for the preparation of liq. chlori. The first three are trade processes, the tanks used in the preparation consisting of Yorkshire flagstones fastened together with iron clamps, and the joints rendered tight with vulcanized caoutchouc.

(1.) By heating a mixture of manganese dioxide and hydrochloric acid. (Scheele.) The reaction takes places in two stages :—

$$(a.)\quad MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$
$$\text{Manganese dioxide} + \text{Hydrochloric acid} = \text{Manganic tetrachloride} + \text{Water.}$$

$$(\beta.)\quad MnCl_4 = MnCl_2 + Cl_2.$$
$$\text{Manganese tetrachloride} = \text{Manganous chloride} + \text{Chlorine.}$$

[To purify the gas it should be passed first through water to absorb HCl, and afterwards through strong sulphuric acid to absorb moisture. It must be collected either by the displacement of air or over hot water. Mercury cannot be used.]

Any oxide will yield chlorine with hydrochloric acid, and may be used in the place of the manganese oxide (*e.g.*, baric or plumbic peroxides), provided its corresponding chlorides are non-existent, or are decomposed at the temperature to which the mixture is subjected.

If oxide of manganese and hydrochloric acid be mixed in the cold, a brown liquid results, which probably contains $MnCl_4$ in solution. If this solution be heated free chlorine will be evolved.

In *Weldon's* process (which is employed in dealing with the "still liquor" of bleaching-powder factories), the $MnCl_2$ formed as above (β) is decomposed by lime ($MnCl_2 + CaO = MnO + CaCl_2$). This MnO is then mixed with more lime, and air blown through the mixture, whereby the MnO is converted into MnO_2, which may be again used for generating chlorine with hydrochloric acid.

It has been suggested to prepare chlorine by heating the dioxide of manganese with a mixture of nitric and hydrochloric acids (Schlösing). Chlorine is evolved, whilst the manganous nitrate formed, yields when heated MnO_2 and nitric acid, which MnO_2 may be again used to decompose fresh hydrochloric acid.

(2.) By heating a mixture of sulphuric acid, manganese dioxide and common salt. In this process (which differs from the former in producing the hydrochloric acid in the same vessel in which the chlorine is generated) the action is more gradual, whilst the whole of the chlorine in the sodic chloride is liberated :—

$$2NaCl + MnO_2 + 3H_2SO_4 = 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2.$$

Sodic chloride + Manganese dioxide + Sulphuric acid = Acid sodic sulphate + Manganese sulphate + Water + Chlorine.

(3.) By passing air and hydrochloric acid gas over red-hot bricks (whereby heating surface is gained), or through red-hot tubes (Oxland, 1847) :—

$$2HCl + \textit{Air}\ (O \text{ and } N_4) = H_2O + Cl_2 + N_4.$$

[It will be remarked that in this process the chlorine is mixed with twice its bulk of nitrogen. For trade purposes this is unimportant.

Any undecomposed HCl evolved may be absorbed by passing the gases through water.]

This process has been improved by Deacon ("Journ. Chem. Soc.," x., 725), who passes the mixed air and hydrochloric acid gas over heated fire-bricks previously soaked in a solution of cupric sulphate or cuprous chloride, and afterwards dried. In this way far less undecomposed HCl escapes. The cuprous chloride first becomes cupric chloride (a), which, by increased heat, again becomes converted into cuprous chloride (β). Thus—

$$(a.)\quad Cu_2Cl_2 + O + 2HCl = 2CuCl_2 + H_2O.$$

Cuprous chloride + Oxygen + Hydrochloric acid = Cupric chloride + Water.

$$(\beta.)\quad 2CuCl_2 = Cu_2Cl_2 + Cl_2.$$

Cupric chloride = Cuprous chloride + Chlorine.

This action, where the simple presence of a third body seemingly determines chemical changes, is an illustration of what is termed *cata-*

lysis (see p. 13), nevertheless the continuous action is more complicated than might be supposed, a series of reactions, resulting in the formation of unstable intermediate compounds, taking place, and as a final act, the formation of the original substance.

(4.) By the action of heat on a mixture of hydrochloric acid and potassic bichromate. (Rogers) :—

$$K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + 3Cl_2.$$

Potassic bichromate + Hydrochloric acid = Potassic chloride + Chromic chloride + Water + Chlorine.

(5.) By the electrolysis of hydrochloric acid, or of an aqueous saturated solution of sodic chloride (see page 20):—

$$2HCl = H_2 \text{ (negative pole)} + Cl_2 \text{ (positive pole)}$$

(6.) By fusing together ammonic nitrate and ammonic chloride. (Maumené) :—

$$4NH_4NO_3 + 2NH_4Cl = 12H_2O + 5N_2 + Cl_2.$$

Ammonic nitrate + Ammonic chloride = Water + Nitrogen + Chlorine.

(7.) By the action of heat on certain chlorides, such as the chlorides of platinum, palladium, or gold. Thus—

(*α*.) $PtCl_4 = PtCl_2 + Cl_2$. (*β*.) $PtCl_2 = Pt + Cl_2$.

(8.) By heating a mixture of magnesic chloride and manganese dioxide. (Binks and Macqueen) :—

$$2MgCl_2 + MnO_2 = 2MgO + MnCl_2 + Cl_2.$$

Magnesic chloride + Manganese dioxide = Magnesic oxide + Manganous chloride + Chlorine.

(9.) By the ignition of anhydrous magnesic chloride in air :—

$$2MgCl_2 + O_2 = 2MgO + 2Cl_2.$$

Magnesic chloride + Oxygen = Magnesic oxide + Chlorine.

(10.) By the action of an acid on an alkaline hypochlorite.

Properties.—(*α*.) *Sensible.*— Chlorine is a yellowish-green gas (χλωρος), having an insupportable odor and a strong burning taste.

(*β*.) *Physiological.*—It is poisonous and intensely irritating, even when largely diluted with air. A bird dies in a 5 per cent. atmosphere. The gas rapidly disorganises all tissues.

(*γ*.) *Physical.*—It has an experimental specific gravity of 2·47, and a theoretical specific gravity of 2·45. Its vapour density at ordinary pressures, when pure, remains constant up to 2712 F. (1600° C.), but if mixed with air so as to lessen the chlorine pressure, a diminution of vapour density, with increased pressure, occurs as the temperature rises, from the partial dissociation of the chlorine molecule (Cl_2) into chlorine atoms (Cl). At 1600° C. this diminution amounts to about 16 per cent.

100 cubic inches, at standard temperature, weigh 76·076 grains, and 1 litre 3·1734 grms. It is, therefore, one of the heaviest bodies, gaseous at ordinary temperatures, known.

A temperature of –130° F. (–90° C.) at ordinary pressures, or a pressure of 6 atmospheres at 32° F. (0° C.), or of 8·5 atmospheres at 54·5° F. (12·5° C.), converts chlorine into a yellowish green liquid, which is not miscible with water. (Sp. Gr. 1·33.) Liquid chlorine boils at –29° F. (–33·6° C.), but it has never been solidified. It is a non-conductor of electricity, and possesses a refractive index lower than that of water. It may be prepared either by heating crystals of the hydrate (Cl_2, $10H_2O$) or of platinic chloride ($PtCl_4$) in one end of a bent and sealed tube, the other end, so constructed as to form a receptacle for the liquid chlorine, being immersed in ice and salt.

If the solar spectrum be passed through chlorine, it will be found that the blue end is cut off and the position of Frauenhofer's lines disturbed. Chlorine does not conduct electricity. It is an electro-negative body, and passes to the + pole of the battery after oxygen and fluorine.

Charcoal at ordinary temperatures absorbs about 200 volumes of chlorine, the gas being disengaged from the carbon by heat.

Draper has stated that chlorine after exposure to sunlight combines with hydrogen more readily than before such exposure, and also that it increases in volume to an extent not accounted for by the simple heating effect of the sun's rays. From these experiments, he has assumed the possibility of an allotropic modification. Roscoe's experiments do not confirm those of Draper.

Solubility in water.—The maximum solubility of chlorine in water occurs at 50° F. (10° C.) :—

At 50° F. (10° C.)	water	absorbs	2·585	times its bulk of the gas.
At 59° F. (15° C.)	”	”	2·368	” ”
At 68° F. (20° C.)	”	”	2·156	” ”
At 86° F. (30° C.)	”	”	1·749	” ”
At 104° F. (40° C.)	”	”	1·365	” ”

Below 50° F. (10° C.) the formation of the hydrate (Cl_2, $10H_2O$) commences, whilst in water at 212° F. (100° C.) no gas dissolves. Chlorine water possesses the general properties of free chlorine, the saturated solution evolving chlorine on exposure to air. Exposed to daylight, the solution decomposes more or less rapidly, according to the intensity of the light (the yellow color of the solution gradually disappearing), whilst in sunlight the decomposition may be as complete as is represented by the equation $H_2O + Cl_2 = 2HCl + O$.

(c.) *Chemical.*—Chlorine is not a combustible gas (*i.e.*, does not burn in air, being incapable of direct combination with oxygen). When largely diluted with air, it supports the combustion of a vigorously-burning taper, the chlorine combining with the hydrogen of the hydro-carbon, and setting free the carbon. It bleaches, without reddening, blue litmus.

If an aqueous solution be cooled to 32° F. (0° C.), or if the gas be passed into water at 32° F., a yellow crystalline hydrate (Cl_2+10H_2O), is formed, containing 27·7 per cent. of chlorine. The foggy appearance of the gas collected on a cold day over very cold water is due to the formation of this compound. The gas clears rapidly on the application of a moderate warmth. Exposed to air, chlorine-hydrate speedily decomposes into chlorine and an aqueous solution of the gas, but if preserved in sealed tubes, it may be sublimed by heat unchanged. At a temperature of 100·4° F. (38° C.) the hydrate decomposes into liquid chlorine and an aqueous solution of the gas.

Action on the non-metals.—With most of the non-metals chlorine combines directly. Phosphorus catches fire in chlorine spontaneously, forming PCl_3. Sulphur burns in it feebly, forming SCl_2 or S_2Cl_2. Selenium, boron, and silicon combine with it when heated. Its union with carbon, nitrogen, and oxygen is indirect only. It does not combine with fluorine.

Combinations with hydrogen.—Chlorine has a very strong affinity for hydrogen. Its oxidizing property depends upon this powerful affinity for the hydrogen of water, oxygen being thereby liberated. A mixture of equal volumes of hydrogen and chlorine, combine *with explosion* by the electric spark, or when exposed to direct sunlight or to any other light (such as the electric arc or the magnesium flame) containing a good supply of actinic rays. The gases unite *quietly* when exposed to the light of a gas-flame or diffused daylight, hydrochloric acid being formed. In the dark, combination does not occur.

Action on hydrogenous compounds.—The following reactions of chlorine on hydrogen compounds should be noted:—

(1.) A taper burns in dilute chlorine with a smoky flame, the chlorine combining with the hydrogen and liberating the carbon. If a jet of chlorine be allowed to play on the flame of a spirit lamp, it becomes luminous, from solid carbon particles being set free. (2.) Turpentine vapor ($C_{10}H_{16}$) catches fire in chlorine, a large quantity of carbon being disengaged ($C_{10}H_{16} + 8Cl_2 = 16HCl + C_{10}$). (3.) If a mixture of chlorine and olefiant gas (C_2H_4) be fired, carbon is set free ($C_2H_4 + 2Cl_2 = 4HCl + C_2$). (4.) A mixture of chlorine and marsh gas (CH_4) under the influence of sunlight forms chloroform ($CHCl_3$) and tetrachloride of carbon (CCl_4). (5.) Ammonia solution is decomposed by chlorine, nitrogen being liberated ($8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$). By its action on a solution of ammonic chloride, chlorine forms the highly explosive body, chloride of nitrogen. (6.) When sulphuretted hydrogen gas is passed into chlorine water, the sulphur is set free, and hydrochloric acid formed. (7.) Water is decomposed by chlorine. Thus, oxygen may be obtained by passing steam and chlorine through a red-hot tube (see page 72).

Action on organic bodies.—The affinity of chlorine for hydrogen renders its action on organic bodies very powerful. These actions may be thus classified—

(1.) *The chlorine may be simply added to the hydrogen compound.* Thus— C_2H_4 (*ethene or olefiant gas*) $+ Cl_2 = C_2H_4Cl_2$ (*ethene chloride*).

(2.) *A portion of the hydrogen may be displaced, but without the substitution of chlorine for it.* Thus—

C_2H_6O (*alcohol*) $+ Cl_2 = C_2H_4O$ (*aldehyd*) $+ 2HCl$.

(3.) *A part or all the hydrogens of a compound may be displaced, chlorine being substituted for them.* The action of chlorine on marsh gas and on acetic acid may be given as illustrations :—

(*a.*) *The action of chlorine on marsh gas* (CH_4) :—

$CH_4 + Cl_2 = CH_3Cl$ (*methyl-chloride*) $+ HCl$.
$CH_4 + Cl_4 = CH_2Cl_2$ (*formyl-bichloride*) $+ 2HCl$.
$CH_4 + Cl_6 = CHCl_3$ (*chloroform*) $+ 3HCl$.
$CH_4 + Cl_8 = CCl_4$ (*tetrachloride of carbon*) $+ 4HCl$.

(*β.*) *The action of chlorine on acetic acid* ($C_2H_4O_2$) :—

$C_2H_4O_2 + Cl_2 = C_2H_3ClO_2$ (*monochloracetic acid*) $+ HCl$.
$C_2H_4O_2 + Cl_4 = C_2H_2Cl_2O_2$ (*dichloracetic acid*) $+ 2HCl$.
$C_2H_4O_2 + Cl_6 = C_2HCl_3O_2$ (*trichloracetic acid*) $+ 3HCl$.

It will be noted that this affinity of chlorine for hydrogen and the universal presence of moisture renders chlorine indirectly a powerful oxidizing agent :—($2H_2O + 2Cl_2 = 4HCl + O_2$.) Thus a solution of chlorine instantly changes sulphurous into sulphuric acid ($H_2SO_3 + Cl_2 + H_2O = H_2SO_4 + 2HCl$).

Some results of this oxidizing action may be noted:—

(1.) *Various chemical combinations may be effected*, as *e.g.* the formation of acetic acid from aldehyd :—

C_2H_4O (*aldehyd*) $+ H_2O + Cl_2 = C_2H_4O_2$ (*acetic acid*) $+ 2HCl$.

(2.) *The bleaching power of chlorine* depends on the action of the nascent oxygen developed as the chlorine combines with the hydrogen of the water. Absolutely dry chlorine has no bleaching action, but in the presence of moisture every organic coloring matter, except carbon, is decolorized. Mineral colors generally are not acted upon. Thus, ordinary writing ink (the black of which is due to an iron salt of an organic acid) is bleached by it, whilst printers' ink (the black of which is due to carbon) remains unaffected. In the case of indigo, which chlorine bleaches readily, it is changed first into isatin, and afterwards into the yellow-tinted chlor-isatin. The following equations represent this action—

(*a.*) C_8H_5NO (*indigo*) $+ H_2O + Cl_2 = C_8H_5NO_2$ (*isatin*) $+ 2HCl$.

(*β.*) $C_8H_5NO_2$(*isatin*) $+ Cl_2 = C_8H_4ClNO_2$(*chlor-isatin*) $+ HCl$.

Further, a coloring matter bleached by chlorine is destroyed, *i.e.,* it cannot be restored by the action of other re-agents, as in the case of a coloring body bleached by sulphurous acid.

(3.) Its *power of disinfection*, depends upon the activity of chlorine in breaking up ammonia, sulphuretted hydrogen, and organic matters generally, and upon the energy of the nascent oxygen set free from its combination with hydrogen in water.

Action on the metals, metallic oxides, etc.—(α.) Its action on all the metals, except iridium, is energetic. Powdered antimony or arsenicum, finely divided iron, Dutch leaf (copper and zinc), etc., fire spontaneously when dropped into chlorine. Melted sodium and potassium also fire spontaneously, forming NaCl and KCl. With respect to sodium, ignition does not occur if the chlorine be perfectly dry, but in the case of potassium it is immaterial whether the gas be dry or moist. (Wanklyn.) Magnesium burns in it, forming $MgCl_2$. Gold (as leaf gold) combines slowly with chlorine, forming $AuCl_3$.

(β.) Metallic oxides, where the affinity between the oxygen and the metal is feeble, are easily decomposed by chlorine. Thus—

$$H_2O + \underset{\text{Mercuric oxide}}{3HgO} + 2Cl_2 = \underset{\text{Mercuric oxy-chloride.}}{2HgO,HgCl_2} + 2HClO.$$

(γ.) Chlorine is absorbed by a solution of caustic potash, potassic chloride and potassic hypochlorite being formed:—

$$Cl_2+2KHO=KCl+KClO+H_2O.$$

Tests.—Its odor, color, and bleaching properties constitute the chief tests for free chlorine. When combined or in a free state, it may be known as follows:—

(1.) *Mercurous nitrate* gives a white precipitate of mercurous chloride or calomel (Hg_2Cl_2), insoluble in nitric acid, and turned black by ammonia.

(2.) *Argentic nitrate* gives a white curdy precipitate (AgCl), soluble in ammonia, and insoluble in nitric acid. *Free* chlorine produces with the argentic chloride, a trace of argentic chlorate:—

$$6AgNO_3 + 3Cl_2 + 3H_2O = 5AgCl + AgClO_3 + 6HNO_3.$$

Fallacies.—Bromides, iodides, and cyanides:—(1.) The *bromide* of silver is of a reddish color. (2.) An *iodide* is known (α) by its action on starch paste, the iodine being set free by the addition of a trace of chlorine water, or (β) by its reaction on palladic nitrate. (3.) A *cyanide* is known by the formation of prussian blue, when acted on by a mixed per- and protosalt of iron.

Estimation.—Chlorine is determined quantitatively as argentic chloride, every 100 parts of which contain 24·74 parts of chlorine.

Uses.—(a.) In *nature*, none.

(b.) In *the arts*, chlorine is largely used as *a bleaching agent* for paper, linen and cotton cloth. Wool and silk fabrics cannot be bleached with chlorine, on account of the injurious action of the gas upon them. For these sulphurous acid is used as a bleach. Chloride of lime, as it is called, is the form in which the chlorine is ordinarily employed. Any acid will liberate the chlorine from this compound. The chlorine employed in its manufacture is usually generated in square tanks, heated by a steampipe, the tanks being constructed of flagstones clamped with vulcanized caoutchouc joints. Chlorine is also used to whiten discolored prints and engravings, on account of its not affecting printers' ink.

After chlorine has been used in any of the above operations, every trace of it must be removed, otherwise the resulting HCl would render the articles brittle. Mere washing for this purpose is insufficient. Hence what is called an "*antichlor*" is employed, such as calcium sulphite (which by the action of chlorine in the presence of water becomes calcium sulphate), or sodium thiosulphate (which under like conditions becomes sulphur and sodium sulphate).

(*c.*) In *medicine*, the dilute gas is used as an inhalation (vapor chlori, B.P.), *i.e.* moist chlorinated lime from which the carbonic acid of the air sets free a little chlorine; and in solution (liquor chlori, B.P.), which, to prevent decomposition, should be preserved in dark blue bottles. When freshly prepared, it contains more than twice (2·3) its bulk of chlorine, and about 0·75 per cent. by weight.

(*d.*) As a *disinfectant* its action depends on its power of breaking up offensive effluvia and miasms. If chloride of lime be used for the sick room, a quarter of a pound should be dissolved in about a gallon of water. A piece of flannel dipped in the *clear* liquor should then be freely exposed to the air of the room, from which, by the action of atmospheric carbonic acid, a small but regular evolution of chlorine, or of an oxide of chlorine, will take place. For active disinfection, some bleaching powder and sulphuric acid or vinegar, or better still, some hydrochloric acid and dioxide of manganese should be mixed on a plate, and the plate placed on a hot brick. The room must then be closed, and left for some hours, everything metallic having been previously removed.

(*e.*) In the laboratory, the oxidizing power of chlorine is often used, protoxides being converted by its action into peroxides, sulphur into sulphuric acid, etc.

COMPOUNDS OF CHLORINE AND OXYGEN.

Chlorine and oxygen are both strongly electro-negative bodies and possess great affinity for hydrogen. Hence their affinity for each other is but slight. They do not combine directly, but in the presence of a third body only, such as a basic oxide (*e.g.*, caustic potash, mercuric oxide, etc.). Further, the compounds formed by their combinations are unstable. Hence, they are powerful oxidizing agents, and in certain instances explosive bodies.

There are four oxygen acids which have been regarded for obvious reasons as a series of oxides of hydrochloric acid.

OXIDES AND ACIDS OF CHLORINE.

Hypochlorous Anhydride	Cl_2O.
Chloric Peroxide	ClO_2.

Hypochlorous Acid	$HClO$.
Chlorous Acid	$HClO_2$.
Chloric Acid	$HClO_3$.
Perchloric Acid	$HClO_4$.

Until lately, the body Cl_2O_3 (chlorous anhydride), was believed to be set free by deoxidizing chloric acid with nitrous anhydride (Millon, 1842). Recent researches, however, have shown that this supposed compound is a mixture of ClO_2 and free chlorine.

Hypochlorous Anhydride ($Cl_2O = 87$) (accurately 86·7).

Molecular weight, 87. *Molecular volume,* $\boxed{\,:\,}$. *Specific gravity* (*Air* = 1) *theoretic,* 3·01. *Liquid boils at* 68° F. (20° C.). 1 *litre weighs* 43·5 *criths* (0·0896 × 43·5) = 3·8976 *grms., and* 100 *cubic inches* 93·22 *grains.*

Synonyms.—*Chlorine monoxide; hypochlorous oxide.*

History.—The fact that when chlorine was combined with an alkali (caustic potash) it would still bleach (constituting the Eau de Javelle) was noted by Berthollet (1785). The use of lime as the absorbent was suggested by Tennant (1798). The constitution of the bleaching compounds was investigated by Balard (1834).

Preparation.—(1.) By passing dry chlorine over dry precipitated mercuric oxide contained in a cold tube. (Pelouze.)

$$HgO + 2Cl_2 = HgCl_2 + Cl_2O.$$

Mercuric oxide + Chlorine = Mercurous chloride + Hypochlorous anhydride.

(2.) By abstracting water from hypochlorous acid, by means of glacial phosphoric acid :—

$$2HClO - H_2O = Cl_2O.$$

Hypochlorous acid — Water = Hypochlorous anhydride.

(3.) By the action of phosphorous oxychloride on potassic chlorite :—

$$2KClO_2 + POCl_3 = KPO_3 + KCl + 2Cl_2O.$$

Potassic chlorite + Phosphorous oxychloride = Potassic phosphate + Potassic chloride + Hypochlorous anhydride.

(4.) Hypochlorous anhydride is believed by some to be produced when hydrochloric acid is added to potassic chlorate in the process of making the euchlorine of Davy, but of this there is much doubt.

Properties.—(*a.*) *Sensible and Physiological.*—A gas of deeper color than chlorine. It has a penetrating odor, a sweet taste, and is intensely suffocating when breathed.

(β.) *Physical.*—Its specific gravity is 3·01. Two volumes of chlorine and one volume of oxygen form two volumes of Cl_2O (water type). 100 cubic inches weigh 93 grains, and 1 litre 3·897 grammes. By pressure, and by the cold of ice and salt, it may be condensed into a red liquid, which boils at —4°F. (—20° C.). Friction or other mechanical means, light, and a very slight heat, such as the warmth of the hand, decompose it with explosion. Water at ordinary temperatures dissolves about 200 times its bulk of the gas, forming a yellow solution, which has an acrid taste (hypochlorous acid).

(γ.) *Chemical.*—It bleaches litmus and indigo more powerfully than chlorine. It is decomposed by a spark. Any substance having an affinity for chlorine or for oxygen, such as sulphur, phosphorus, or the alkaline metals, decompose it with explosion. Hydrochloric acid effects its decomposition ($2HCl + Cl_2O = H_2O + 2Cl_2$).

Hypochlorous Acid ($HClO = 52{\cdot}5$).

Synonym.—*Hydric hypochlorite.*

Preparation.—(1.) By the action of water on hypochlorous anhydride:—

$$Cl_2O + H_2O = 2HClO.$$

Hypochlorous anhydride + Water = Hypochlorous acid.

(2.) By passing air, charged with hydrochloric acid gas, through a solution of potassic permanganate acidulated with sulphuric acid, and heated on a water bath. The product is to be collected by distillation. In this reaction HClO is formed from HCl, by direct oxidation ($2HCl + O_2 = 2HClO$).

(3.) By mixing together mercuric oxide, water, and chlorine. The liquid must be decanted from the insoluble oxychloride.

$$3HgO + H_2O + 2Cl_2 = 2HgO, HgCl_2 + 2HClO$$

Mercuric oxide + Water + Chlorine = Mercuric oxychloride + Hypochlorous acid.

(4.) By distilling a hypochlorite with an oxy-acid:—

$$CaCl_2O_2 + H_2SO_4 = CaSO_4 + 2HClO.$$

Calcic hypochlorite + Sulphuric acid = Calcic sulphate + Hypochlorous acid.

(5.) By saturating a solution of bleaching powder (or baryta water) with chlorine, then passing a current of air through the solution, and finally distilling.

(6.) By passing chlorine gas through a solution of an alkaline carbonate, sulphate or phosphate, etc., or through water containing finely divided calcium carbonate in suspension. (Williamson.)

(α.) $CaCO_3 + H_2O + 2Cl_2 = CaCl_2 + CO_2 + 2HClO.$

Calcic carbonate + Water + Chlorine = Calcic chloride + Carbonic acid + Hypochlorous acid.

(β.) $Na_2SO_4 + H_2O + Cl_2 = NaCl + NaHSO_4 + HClO.$

Sodic sulphate + Water + Chlorine = Sodic chloride + Acid sodic sulphate + Hypochlorous acid.

Properties.—(α.) *Sensible.*—A yellowish-red, chlorine-smelling liquid, having an acrid but not a sour taste.

(β.) *Physiological.*—It acts as an intense irritant poison and browns the skin.

(γ.) *Physical.*—It boils at 19° F. (—7° C.), giving off a heavy yellow vapor. It is decomposed into chlorine and chloric acid by the action of light. The dilute aqueous solution can be distilled without decomposing.

(δ.) *Chemical.*—The gas given off when the acid is heated is very unstable and highly explosive. The acid has powerful oxidizing properties. Its intensity as a bleaching agent is double that of the chlorine it contains, inasmuch as it evolves double the quantity of oxygen (which in the nascent state is the true bleaching agent) set free by ordinary chlorine. Thus—

(α.) $2Cl_2 + 2H_2O = 4HCl + O_2$ (action of common chlorine).
(β.) $2HClO = 2HCl + O_2$ (action of hypochlorous acid).

It is decomposed by carbon, iodine, sulphur, selenium, phosphorus, arsenic, and antimony; carbonic, iodic, sulphuric, selenic, phosphoric, arsenic, and antimonic acids being respectively formed.

If a piece of ammonic chloride be placed in the acid, the oily and highly explosive chloride of nitrogen is formed.

It is a weak acid. Its salts, when moist, may be decomposed even by the carbonic acid of the air.

If the acid or any of its salts be heated with hydrochloric acid, both acids are decomposed:—

$$HCl + HClO = H_2O + Cl_2.$$

Action on the metals.—This varies in a remarkable manner. *Iron* combines with the oxygen of the acid, and sets free chlorine. *Silver* combines with the chlorine of the acid, and sets free oxygen. *Copper* and *mercury* combine both with the chlorine and the oxygen.

To distinguish an hypochlorous acid solution from one of chlorine, shake up with mercury. With the hypochlorous acid solution a white precipitate is produced, soluble in hydrochloric acid (HgO, $HgCl$), whilst with the chlorine solution a white precipitate is formed ($Hg_2 Cl_2$) insoluble in hydrochloric acid.

Action on metallic compounds.—Plumbic oxide combines with the oxygen of the acid, forming PbO_2, and sets free chlorine. Argentic oxide combines with the chlorine and sets free oxygen ($Ag_2O + 2HClO = 2AgCl + H_2O + O_2$). Argentic chloride, by its presence alone, and without being itself decomposed, sets free both the oxygen and the chlorine, in a gaseous form, from the acid.

On several organic bodies the acid acts vigorously. Thus, urea is broken up by its action:—

$$CN_2H_4O + 3HClO = CO_2 + 3HCl + 2H_2O + N_2.$$

Urea + Hypochlorous acid = Carbonic anhydride + Hydrochloric acid + Water + Nitrogen.

The acid is monobasic, and forms, with metallic oxides and hydrates, the salts known as hypochlorites, which are of great importance in the arts ($KHO + HClO = KClO + H_2O$). "Chloride of lime," prepared by bringing chlorine into contact with recently-slaked lime, may be considered as a calcic chloride ($CaCl_2$) mixed with calcic hypochlorite ($CaCl_2O_2$). From the mixture, however, pure calcic hypochlorite cannot be separated.

Chlorous Acid ($HClO_2 = 68{\cdot}5$).

Preparation.—By the decomposition of lead chlorite.

Properties.—The acid is unstable. It neutralises caustic alkalies, but does not decompose alkaline carbonates. It is decomposed even by carbonic anhydride. It is a powerful oxidizing and bleaching agent, and acts on all metals, forming chlorates and chlorides. It is pre-ipitated as plumbic or argentic chlorite with plumbic or argentic itrate. It forms salts called *Chlorites*. (*See* CHLORITES.) The hlorites may be known from hypochlorites by their bleaching ower not being destroyed by the action of nitric acid and arsenious nhydride.

Chloric Peroxide, ClO_2 (Cl_2O_4).*

olecular weight, 67·5. *Specific gravity, theoretic*, 2·335; *observed*, 2·3227. *Boiling Point*, 68° F. (20° C.). 1 *litre weighs* (0·0896 × 33·75) 3·0248 *grm., and* 100 *cubic inches*, 72·226 *grains.*

Synonyms.—*Peroxide of Chlorine; Chloric dioxide; Hypochloric cid; Perchloric oxide; Chlorine peroxide.*

History.—Discovered by Davy in 1815.

Preparation.—1. By heating a mixture of sulphuric acid and otassic chlorate. [The gas must be collected by displacement.]

$$KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + 2ClO_2$$

otassic hlorate + Sulphuric acid = Potassic perchlorate + Hydric potassic sulphate + Water + Chloric peroxide.

2. By heating a mixture of oxalic acid and potassic chlorate to 149° (65° C.). (Calvert.)

$$ClO_3 + 2H_2C_2O_4 = K_2C_2O_4 + 2H_2O + 2CO_2 + 2ClO_2$$

otassic lorate + Oxalic acid = Potassic oxalate + Water + Carbonic acid +. Chloric peroxide.

---

* The formula Cl_2O_4 is probably correct for low temperatures, but seeing that at linary temperatures the vapor density is 33·7 (H = 1), the molecule is more correctly ted us ClO_2 (67·5).

Properties.—(α.) *Sensible and Physiological.*—A deep yellow-green gas, having a strong chlorine odor and a sweet taste. It is excessively irritating.

(β.) *Physical.*—It has a specific gravity of 2·32; 100 cubic inches weigh 72·226 grains. By slight pressure, or by a cold of —4° F. (—20° C.), the gas condenses into a red explosive liquid, which boils at 48·2° F. (9° C.), and freezes at —108·4° F. (—79° C.) At a heat of 140° F. (60° C.) or with an electric spark, it explodes, the resulting gases occupying a volume one-third greater than the original gas. It may be preserved in the dark, but is decomposed by light. Water at 40° F. (4° C.) dissolves 20 times its bulk. At lower temperatures a crystalline hydrate is formed.

(γ.) *Chemical.*—It is a powerful oxidizing and bleaching agent. Its action on many bodies, such as mercury, phosphorus, sugar, ether, and turpentine, is energetic, most of them firing spontaneously. It neither forms an acid nor salts. It is absorbed, however, by alkaline solutions, a chlorite and a chlorate being formed. Thus—

$$Cl_2O_4 + 2KHO = KClO_2 + KClO_3 + H_2O.$$

Chloric peroxide + Potassic hydrate = Potassic chlorite + Potassic chlorate + Water.

Chloric Acid ($HClO_3$ = 84·5).

Synonyms.—*Oxymuriatic acid; hydric chlorate.*

History.—Discovered by Chenevix (1802). Its properties were studied by Gay Lussac (1814).

Preparation.—(1.) A large excess of chlorine is first passed into a strong solution of potassic hydrate, thus producing a potassic chlorate. This is decomposed (the potassic chloride being previously separated by crystallization) with hydrofluosilicic acid:—

(α.) $6KHO + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$

Potassic hydrate + Chlorine = Potassic chloride + Potassic chlorate + Water.

(β.) $2KClO_3 + H_2SiF_6 = 2HClO_3 + K_2SiF_6.$

Potassic chlorate + Hydrofluosilicic acid = Chloric acid + Potassic fluosilicate.

(It is, perhaps, best to form a baric chlorate, and to decompose this with its equivalent of sulphuric acid ($BaCl_2O_6 + H_2SO_4 = 2HClO_3 + BaSO_4$). After filtering off the baric sulphate, the acid filtrate must be carefully concentrated by evaporation in vacuo over sulphuric acid, until it has a specific gravity of 1·28, when the liquid contains about 40 per cent. of chloric acid. The residue has the formula $HClO_3 + 7H_2O$. Beyond this point of concentration the acid undergoes decomposition, forming perchloric acid with evolution of oxygen and chlorine.)

Properties. — (α.) *Sensible and Physiological.* — A syrupy liquid, having a strong chloroid smell, a very acid taste and reaction, and a powerful corrosive action on the body.

(β.) *Physical.*—Light after some time decomposes it. It is freely soluble in water. A heat of 100° F. (38° C.) breaks it up into oxygen, chlorine, perchloric acid, and water. Thus—

$$\underset{\text{Chloric acid}}{3HClO_3} = \underset{\text{Perchloric acid}}{HClO_4} + \underset{\text{Water}}{H_2O} + \underset{\text{Oxygen}}{2O_2} + \underset{\text{Chlorine.}}{Cl_2.}$$

(γ.) *Chemical.*—Chloric acid is a powerful acid, and chars or even fires paper and other organic bodies. It rapidly oxidizes organic matter, but it does not bleach readily. It is monobasic, like nitric acid. The anhydride has not been isolated. It forms salts called chlorates, which are largely used both in medicine and in the arts. The acid itself has no uses.

Perchloric Acid ($HClO_4$).

Molecular weight, 100·5. *Specific gravity*, 1·782.

Synonyms.—*Hydric perchlorate.*

History.—Discovered by Count Stadion (1814).

Preparation.—(1.) By distilling potassic perchlorate, with three times its weight of sulphuric acid:—

$$\underset{\text{Potassic perchlorate}}{2KClO_4} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Perchloric acid}}{2HClO_4} + \underset{\text{Potassic sulphate.}}{K_2SO_4.}$$

The distillate solidifies when it is combined with water, forming $HClO_4,H_2O$. If this crystalline body be redistilled, it yields at 230° F. (110° C.), a pure acid, and at higher temperatures, a solution boiling at 397·4° F. (203° C.). (Roscoe.)

(2.) By the action of heat on chloric acid, we obtain perchloric acid, together with chlorine, oxygen and water. (*See* CHLORIC ACID.)

Properties.—(α.) *Sensible and Physiological.*—A colorless liquid, having a sour taste even when very dilute. It produces frightful burns when applied to the skin. It turns yellow by keeping, from the liberation of the oxides of chlorine.

(β.) *Physical.*—A volatile, slightly yellow, mobile liquid. It has a specific gravity of 1·782 at 60° F. (15·5° C.). It remains liquid at —31° F. (—35° C.), and boils at 230° F. (110° C.). It is very hygroscopic.

(γ.) *Chemical.*—The anhydride is unknown. When very dilute it reddens litmus, but it does not bleach vegetable colors. In this dilute form, it is the most stable of the chlorine oxides. It dissolves iron and zinc, setting free hydrogen. The pure acid is one of the most powerful oxidizing bodies known, an explosion resulting when a single drop is brought into contact with any organic substance. Dropped on the skin, it causes burns of great severity. In sealed tubes, it undergoes spontaneous decomposition and bursts the tubes. It decomposes when distilled. It forms with water a white, silky, crystalline, deliquescent hydrate ($HClO_4, H_2O$) (crystals of Serullas). This hydrate fumes in the air and fuses at 122° F. (50° C.). It is decomposed by a heat of 230° F. (110° C.) into the pure acid ($HClO_4$) which distils over, another hydrate, a thick oily liquid, having the composition ($HClO_4$, $2H_2O$), remaining in the retort. This aquate is not volatile at a lower temperature than 397° F. (203° C.).

The acid is monobasic, and forms salts (which are soluble), called perchlorates ($M'ClO_4$).

Euchlorine.—There are several compound oxides of chlorine, the most important of which is *euchlorine.* This was discovered by Davy, and is prepared by heating together hydrochloric acid and a chlorate. It was supposed by Davy to be a distinct oxide, but it is probably a mixture of chlorine and chloric peroxide. It is a yellow explosive gas.

BROMINE (Br.).

Atomic weight, 80, (more accurately, 79·75). *Molecular weight,* 160. *Molecular volume* $\boxed{\quad|\quad}$. *Atomicity monad* (HBr—KBr). *Specific gravity of vapor* (*Air*=1), *theoretic and observed,* 5·54. *Specific gravity of liquid* (*Water* =1) *at* 32° F., 3·187. *Fuses at* —12° F. (—24·5° C.). *Boils at* 145·4° F. (63·0° C.).

Synonyms.—*Muride* (*muria,* brine), Balard (1826); *Bromine* (*βρῶμος,* fetid), Gay Lussac.

History.—Bromine was discovered by Balard, of Montpellier, in August, 1826, in "bittern," the mother liquor of sea water, and was at the time supposed to be a compound of chlorine and iodine. Afterwards Balard, Lœwig, and Serullas together, proved its elementary nature.

Natural History.—It never occurs in nature in a free state. (*a.*) *In the mineral kingdom* it is invariably found in company with chlorine compounds. Sea water contains 0·9 to 1·25 grains of $MgBr_2$ per gallon. The Dead Sea water is specially rich in bromine compounds. So also are the mineral springs of Kreutznach, Kissengen, Kurshall, etc. Bromine is also found in the potash beds at Stassfürth, and mineralized with silver, zinc, and cadmium. It is found in most samples of rock-salt, and also in coal. (Bussy.) (*β.*) *In the vegetable kingdom* it is found more or less in all sea plants; and (*γ.*) *in the animal kingdom* it is found in sponges, liver of cods, etc.

Preparation.—As a laboratory process, bromine may be prepared (like chlorine) by heating a mixture of manganese dioxide and sulphuric acid with a bromide ($2NaBr + MnO_2 + 3H_2SO_4 = Br_2 + 2HNaSO_4 + MnSO_4 + 2H_2O$). Commercially, bromine is usually obtained from the mother liquor of the springs of Kreutznach, Schönbeck, etc.

(1.) *The old process used in its preparation was as follows:*—

(*a.*) Chlorine (avoiding great excess, otherwise a chloride of bromine might be formed) is first added to the liquor to set free the bromine:—

$$2KBr + Cl_2 = 2KCl + Br_2.$$

(*b.*) The solution is then shaken up with ether. After standing, the ethereal layer containing the bromine is decanted.

(*c.*) Caustic potash is now added to the bromine solution, and heat applied, whereby the bromine is converted into potassic bromide and potassic bromate—

$$6KHO + 3Br_2 = 5KBr + KBrO_3 + 3H_2O.$$

Potassic hydrate + Bromine = Potassic bromide + Potassic bromate + Water.

(*d.*) The residue is now ignited, in order to convert the potassic bromate into potassic bromide:—

$$2KBrO_3 = 2KBr + 3O_2.$$

(*e.*) The potassic bromide is dissolved in water, and heated in a retort with manganese dioxide and sulphuric acid, when bromine distils over—

$$2KBr + 3H_2SO_4 + MnO_2 = 2HKSO_4 + MnSO_4 + 2H_2O + Br_2.$$

Potassic bromide + Sulphuric acid + Manganese dioxide = Potassic sulphate + Manganous sulphate + Water + Bromine.

(*f.*) The bromine is then re-distilled with calcic chloride in order to free it perfectly from water, and the iodine precipitated as subiodide of copper. To separate the chloride of bromine, the vapors coming from the still are imperfectly cooled, the more volatile bromous chloride thus passing into a second receiver. To free it from chlorine, it is again distilled over potassic bromide, which is converted by any chlorine present into potassic chloride. Another method is to form barium salts, and treat with alcohol, which dissolves the bromide without dissolving the chloride.

(2.) *The process* of Desfosses, as modified by Mohr and Lœwig, consists in distilling the mother liquor at once with an equivalent of manganese dioxide and dilute sulphuric acid in stone vessels heated with steam, the distillate being afterwards rectified with calcic chloride.

Properties.—(*a.*) *Sensible and Physiological.*—Bromine is a heavy, opaque, dark red liquid, evolving red fumes at ordinary temperatures. It is the only liquid non-metallic element, mercury being the only liquid metallic element. Its odour is fœtid and irritating, and its taste acrid and caustic. It stains the skin a permanently yellow color. It is an active poison.

(β.) *Physical.*—Liquid bromine has a specific gravity of 3·187 at 32° F. (0° C.). The vapor is evolved at ordinary temperature, and has a specific gravity of 5·54. At high temperatures, the vapor density diminishes, the molecules undergoing partial dissociation into atoms. It boils at 145·4° F. (63° C.), and freezes to a brown crystalline metallic-looking solid at —12° F. (—24·5° C.). 1 part of bromine is soluble in 31 parts of water at 59° F. (15° C.), the solution having a specific gravity of 1·024. The solution is permanent in the dark, but rapidly decomposes under the influence of sunlight, oxygen being set free, and hydrobromic acid formed. It is also soluble in alcohol, ether, and bisulphide of carbon, the two latter being capable of separating it from its aqueous solution.

(γ.) *Chemical.*—The chemical properties of bromine are in many respects similar to, although less active than, those of chlorine. As an oxidizing agent it bleaches litmus and indigo in the presence of water. A taper introduced into the concentrated vapor burns badly with a smoky flame. Phosphorus and some of the metals (as potassium) take fire when brought into contact with it. With sodium it does not combine below 392° F. (200° C.). Its affinity for oxygen and carbon is as slight as is that of chlorine. Turpentine vapor decolorizes bromine vapor, hydrobromic acid being formed. Here (like chlorine) its affinity for, and its power of displacing hydrogen, are to be noted. It will not, however, combine with hydrogen by mere exposure to the sun's rays. It rapidly attacks organic matters, staining them a yellow colour. It combines with all elementary bodies, forming bromides. It combines with water at the freezing point, forming a hydrate (Br_2, $10H_2O$) which splits up into bromine and water at 59° F. (15° C.).

Tests.—(α.) *In a free state.*—Bromine is set free from its compounds by chlorine. It may be known by its red color, and by forming a yellow compound with starch.

(β.) *In combination.*—(1.) *Plumbic acetate* gives a white precipitate of plumbic bromide ($PbBr_2$). (2.) *Argentic nitrate* gives a yellowish-white precipitate of argentic bromide ($AgBr$) which is insoluble in dilute nitric acid, and of difficult solubility in dilute ammonia.

Uses.—In *the arts*, bromine is used in photography. In *medicine*, the bromide of ammonium (NH_4Br) (ammonii bromidum, B.P.), the ferrous bromide ($FeBr_2$), the potassic bromide (KBr), as well as a solution of bromine (10 minims in 5 ozs. of water) are officinal.

Bromine is a disinfectant, its power being dependent on its affinity for hydrogen, and its consequent oxidising properties.

COMPOUNDS OF BROMINE AND OXYGEN.

There are two bromine acids, viz., hypobromous and bromic, and, possibly, a third, the perbromic. The anhydrides are unknown.

(1.) $HBrO$ Hypobromous acid.
(2.) $HBrO_3$ Bromic acid.
(3.) $HBrO_4$ Perbromic acid (?)

Hypobromous Acid ($HBrO$).

A solution of this acid may be formed, like hypochlorous acid (page 97), either by agitating mercuric oxide with bromine water

(Balard) ($2HgO + 2Br_2 + H_2O = 2HBrO + Hg_2 Br_2O$), or by adding bromine to an argentic nitrate solution (Dancer). It is a yellow liquid, easily decomposed by heat, but may be distilled in vacuo at a temperature of 104° F. (40° C.). It oxidizes and bleaches powerfully. It forms salts, called hypobromites (*see* Index). Added to milk of lime, bromine forms an analogous compound to bleaching powder.

Bromic Acid ($HBrO_3$).

The anhydride of bromic acid is unknown.

Preparation.—It may be prepared in a similar manner to chloric acid; also by passing chlorine through bromine water ($Br_2 + 5Cl_2 + 6H_2O = 2HBrO_3 + 10HCl$), also by the decomposition of silver bromate with bromine ($5AgBrO_3 + 3Br_2 + 3H_2O = 5AgBr + 6HBrO_3$), and also by decomposing baric bromate with sulphuric acid ($BaBr_2O_6 + H_2SO_4 = 2HBrO_3 + BaSO_4$).

Properties.—An acid liquid, first reddening and afterwards bleaching blue litmus. At 212° F. (100° C.) it splits up into bromine and oxygen. Reducing agents (as H_2S and SO_2) decompose it. Hydrobromic, hydrochloric, and hydriodic acids also decompose it, water and bromine being formed in the first case, and chloride or iodide of bromine in the two last. It forms salts, called bromates. (*See* Index.)

Perbromic Acid ($HBrO_4$).

This is said to be formed by adding bromine to a solution of perchloric acid (Kämmerer). It is described as a colorless, oily liquid, and the most stable of the oxides of bromine.

COMPOUND OF BROMINE AND CHLORINE.

Bromous Chloride ($BrCl_3$?)

Is prepared by passing chlorine through liquid bromine (Balard). It is a reddish, volatile, very unstable, pungent liquid, soluble in water, the solution possessing considerable bleaching power. On cooling, a crystalline hydrate separates out.

IODINE (I).

Atomic weight, 127 (more accurately, 126·53). *Molecular weight,* 254. *Molecular volume,* ☐☐. *Atomicity monad* ('), (HI); *occasionally triad* (ICl_3). *Specific gravity of solid iodine,* 4·947; *of vapour, theoretic* 8·801; *observed,* 8·716. *Melts at* 225° F. (107° C.), *and boils at* 347° F. (175° C.).

History.—Iodine was discovered by Courtois (1812), a French saltpetre manufacturer, on adding sulphuric acid to the waste liquor of kelp. Courtois gave some of it to Desormes and Clement, who published their researches respecting it (1813). It was further examined by Vauquelin, and also by Davy and Gay Lussac (1813 and 1814). The word ἰώδης signifies "violet-colored."

Natural History.—It never occurs in nature in a free state. (*a.*) In the *mineral kingdom* iodine is found in *sea water* as calcic iodide, but to a less extent than the bromine compound (1 in 250,000 : Sonstadt). It is supposed to be the active principle of many *mineral springs*, where it is present in combination with potassium, sodium, and magnesium. The spring at Rey, near Freistadt, contains 8·19 parts, and that at Halles 4·26 parts of magnesic iodide in 100,000 of water. It is also found in the Bath, the Cheltenham, the Leamington, and the Bonnington springs. It is found mineralised with zinc (Silesian ore), lead, mercury, and silver (Mexican ore). It is found in rock salt, in many limestones and dolomites, in Chili nitre (and hence occasionally constitutes an impurity of nitric acid), and occasionally in coal. (*β.*) In *the vegetable kingdom* it is found in sea-weeds as an alkaline iodide, extracted by them from sea-water in quantities varying from 0·01 to 0·5 per cent. The Laminaria digitata is one of the richest.

	Iodine in 100 parts of dried plant.
Laminaria digitata	0·47
Laminaria saccharina	0·16
Fucus vesiculosus	0·01
Fucus nodosus	0·04

Scotch and Irish sea-weeds contain more iodine than English sea-weeds. It is said to be present in the fresh-water plants that grow in running streams (Chatin). (*γ.*) In the *animal kingdom*, it is found in marine animals, and notably in sponges, oysters, etc. It is an invariable constituent of cod liver oil (0·04 to 0·32 per cent.).

Preparation.—(1.) *Process of Wollaston, as modified by Whytelaw* (*a.*) The sea-weeds found on the Scotch coast (specially the laminaria digitata) are collected during the summer months and at low tide, dried by exposure, and then burnt without flame, in order to prevent, as far as possible, any loss of sodic iodide. Sometimes it is carbonized in retorts. The ash constitutes what is called " kelp " in Scotland, and " varec " in Normandy. A ton of good kelp made from the laminaria digitata will yield from 10 lbs. to 15 lbs. of iodine.

(*b.*) The kelp is first lixiviated with boiling water, whereby about 50 per cent. of solid matter is dissolved, consisting of sodic carbonate, sulphate, sulphite, and sulphide, besides sodic, potassic and magnesic chlorides and iodides.

(*c.*) The solution is filtered and afterwards evaporated to a smaller bulk, in order to separate the sodic carbonate (Scotch soda). It is afterwards still further evaporated so as to separate the sodic sulphate and chloride.

(*d.*) The residual liquor (sp. gr. 1·33 = *iodine ley*) is now mixed with about one-eighth its bulk of oil of vitriol, and allowed to stand for 24 hours, whereby carbonic and sulphurous acids, together with sulphuretted hydrogen, are evolved, and sodic sulphate with much free sulphur separated.

(*e.*) The liquid is then filtered and put into a leaden still (iodine still) with manganese dioxide, and heated to a temperature not exceeding 212° F. (100° C.). In this way the formation of chlorine is prevented, and the iodine obtained as a sublimate:—

$$\underset{\text{Sodic iodide}}{2NaI} + \underset{\text{Manganese dioxide}}{MnO_2} + \underset{\text{Sulphuric acid}}{2H_2SO_4} = \underset{\text{Sodic sulphate}}{Na_2SO_4} + \underset{\text{Manganic sulphate}}{MnSO_4} + \underset{\text{Water}}{2H_2O} + \underset{\text{Iodine.}}{I_2.}$$

(*f.*) The iodine is now purified by resublimation. Commercial iodine generally contains more or less chloride, cyanide, and bromide of iodine.

(2.) A second process occasionally adopted in the preparation of iodine, is throwing it down with a subsalt of copper, as a biniodide of copper. In practice, cupric and ferrous sulphate are mixed with the iodine ley. The subiodide of copper (Cu_2I_2) formed is then distilled with manganese dioxide and sulphuric acid, whereby the iodine is liberated—

$$Cu_2I_2 + 2MnO_2 + 4H_2SO_4 = 2CuSO_4 + 2MnSO_4 + 4H_2O + I_2.$$

(3.) *Emil Bechi's Process* (Prize Essay, Florence, 1849). When the solutions are very poor in iodide, Bechi sets free the iodine with nitro-hydrochloric acid, and then filters the liquid through recently ignited lampblack. The lampblack is then treated with a potash solution, and the washings evaporated to dryness, the iodine from the solid residue being afterwards liberated by distillation with manganese dioxide and sulphuric acid.

(4.) The iodine is sometimes thrown down from the solution by first adding a little chlorine or nitro-hydrochloric acid, and afterwards raw starch, which sinks to the bottom, carrying the iodine with it.

(5.) The iodine, after being liberated with chlorine, or with sulphuric acid containing some nitric acid, is sometimes extracted from the aqueous solution by shaking it up with benzol or petroleum. The benzol solution is then treated with a solution of potash, when potassic iodide and potassic iodate are formed (α), from which the iodine may be precipitated with hydrochloric acid (β).

(α.) $6KHO + 3I_2 = 5KI + KIO_3 + 3H_2O.$

(β.) $5KI + KIO_3 + 6HCl = 6KCl + 3H_2O + 3I_2$

(6.) *In Stanford's process* for the preparation of iodine, the winter weeds (said to contain the most iodine) are dried under cover, submitted to hydraulic pressure, and heated in iron retorts, the gas set free, being collected and utilised.

Properties.—(α). *Sensible.* —Iodine is a black solid, having considerable metallic lustre, and crystallizing in acute rhombic octahedra. Its odor is peculiar, and its taste acrid. It stains the skin yellow. The vapor has a bright violet color.

(β.) *Physiological.*—An irritant and caustic poison. The vapor is irritating to the lungs, but when largely diluted with air, it has been found in certain cases to act beneficially (vapor iodi, B.P.).

(γ.) *Physical.*—Solid iodine has a specific gravity of 4·947 at 62·6° F. (17° C.), and the vapor 8·716. The vapor of iodine is the heaviest vapor known, 100 cubic inches weighing 275·16 grains. At 2552° F. (1400° C.) the vapor has about two-thirds the vapor density that it has at 700° C. some of the molecules being split up at this higher temperature into atoms. Iodine volatilizes unchanged, both at ordinary and at high temperatures. It fuses at 235·4° F. (113° C.). It boils, when perfectly dry, at 347° F. (175° C.), but when distilled with water it volatilizes at 212° F. (100° C.). The specific heat of the solid is 0·03412, and of the liquid 0·10882 (Regnault). It is a non-conductor of heat and electricity. Its solution in carbon disulphide is found to be opaque to light rays, but transparent to heat rays. Iodine is dichroic. If the vapor be freely diluted with air, it transmits the red and blue rays of light, and absorbs the green ; but the concentrated vapor absorbs the red rays also, the blue only being transmitted. Seven thousand parts of water at 60° F. (15·5° C.), dissolve one part of iodine, forming a pale brown liquid, which, in the presence of oxidizable matter, rapidly decomposes, hydriodic acid being formed. Hot water dissolves a larger quantity. The presence of saline matters, of hydriodic acid, and specially of potassic iodide, greatly facilitates solution. Lugol's solution (liquor iodi, B.P.) consists of 20 grs. of iodine, and 30 of potassic iodide in 1 oz. of water. Iodine is far more soluble in alcohol and ether than in water. If water be added to its solution in ether or in alcohol, some of the iodine will be precipitated. A spirituous solution with potassic iodide, forms the tinctura iodi (B.P.). It is even more soluble in chloroform, in benzol, in carbon disulphide (which solution is diathermous), and in carbon tetrachloride, its solution in these liquids being black, and depositing iodine on evaporation. A very dilute solution of iodine in chloroform or in bisulphide of carbon exhibits a strong pink or purple color.

(δ.) *Chemical.*—An aqueous solution of iodine bleaches litmus and indigo slightly. A taper introduced into iodine-vapour is immediately extinguished. Iodine combines more readily with oxygen than either chlorine or bromine. It forms iodic acid when boiled with nitric acid, neither chlorine nor bromine being oxidized when similarly treated. Nevertheless, direct union between oxygen and iodine cannot be effected. Iodine expels chlorine from the chlorates ($2KClO_3+I_2=2KIO_3+Cl_2$), but both chlorine and bromine displace iodine from its combination with the metals ($2KI+Cl_2=2KCl+I_2$).

Iodine forms several compounds with chlorine. Phosphorus fires spontaneously when brought into contact with iodine. It combines with sulphur, forming a black crystalline body (S_2I_2), used in medicine. Its action on hydrogen is not intense, presenting, in this respect, a marked contrast both to chlorine and bromine. Although the metals generally combine directly with iodine, its action upon them is weaker than that of either chlorine or bromine. Hence it may be displaced by them. Antimony fires when thrown into iodine gas, and mercury vapor combines with heated iodine. It combines actively with potassium, whilst it may be heated with sodium without alteration. If iodine and iron suspended in water, be heated together, a colourless iodide of iron is formed, a compound used in medicine (ferri iodidum, FeI_2) as a pill (pilula ferri iodidi) and syrup (syrupus ferri iodidi). Iodine forms no definite hydrate with water.

Potash decolorizes an iodine solution ($3I_2+6KHO=6KI+KIO_3+3H_2O$).

As regards its action on organic bodies, it will sometimes be found to combine with the organic body, and sometimes to oxidize it by combining with hydrogen and setting free oxygen. But it never displaces hydrogen directly, although it may at times indirectly.

Tests.—(*a.*) *In a free state only.*—It changes starch a blue color (iodide of starch). [This action of starch on free iodine was discovered by Colin and Gaultier de Claubry. 1 part of iodine in a million parts of water may be detected by this means.] Note in respect of this reaction that—

(1.) Combined iodine is unaffected by starch.

(2.) Iodine when present in combination may be set free by the addition of fuming nitric acid, which converts the iodide into a nitrate, the hydriodic acid produced being decomposed by the nitric peroxide of the fuming acid ($4HI+N_2O_4=2NO+2H_2O+2I_2$), or it may also be set free by the addition of *a trace* of chlorine water, when the blue iodide of starch is formed ($2KI+Cl_2=2KCl+I_2$).

(3.) If too much chlorine be added to the solution, it will bleach the blue iodide of starch, and thus the reaction be obscured ($I_2+6H_2O+5Cl_2=2HIO_3+10HCl$).

(4.) The color may be partially restored by adding a trace of sulphurous acid to the solution ($2HIO_3+4H_2O+5SO_2=5H_2SO_4+I_2$).

(5.) But if an excess of sulphurous acid be added, the color will again disappear ($I_2+2H_2O+SO_2=2HI+H_2SO_4$).

(6.) The color of the blue iodide of starch disappears on heating the solution to 177° F. (80° C.), but on cooling the color is partially restored. If the liquid be boiled, the color does not re-appear.

(7.) The blue color is also destroyed by the addition of alkalies.

If, after the iodine has been set free, the liquid be well shaken with chloroform, it will, on settling, exhibit the characteristic pink colour.

Iodine turns meconine a blue color.

(*b.*) *In combination.*—The following salts give precipitates with the iodides, as follows : *Plumbic acetate,* a yellow ; *argentic nitrate,* a yellowish white ; *mercuric chloride,* a red ; *palladic nitrate,* a brown (1 in 50,000). With *a little chlorine water and starch,* a blue color is produced.

Uses.—*In the arts.*—Iodine is used in photography, and also in the laboratory as a test reagent for starch. *In medicine* it is used as a resolvent. Courdet of Geneva first suggested the use of the ashes of sponge as a curative agent. It is employed officinally in various forms and combinations, such as potassic iodide, liquor iodi, unguentum iodi, and tinctura iodi, the iodide of sulphur being also used as an unguent, and the iodide of iron as a pill and syrup. As a disinfectant its action is powerful.

COMPOUNDS OF IODINE AND OXYGEN.

Two compounds of iodine and oxygen at most (viz., I_2O_5, iodic anhydride, and I_2O_7), and probably only one (viz., I_2O_5) have been prepared.

Iodic Anhydride	I_2O_5.
	I_2O_7(?).
Iodic Acid	HIO_3.
Periodic Acid	HIO_4.

Iodic Anhydride (I_2O_5).

I_2O_5 is formed by the action of heat (170° C.) on iodic acid ($2HIO_3=I_2O_5+H_2O$). This serves to illustrate the greater affinity of oxygen for iodine, than for chlorine or for bromine. Iodic anhydride has a specific gravity of 4·48. It is very soluble in water. At a temperature of 698° F. (370° C.) it is decomposed into oxygen and iodine. With dry HCl, dry I_2O_5 yields iodine trichloride, chlorine and water ($I_2O_5+10HCl=2ICl_3+2Cl_2+5H_2O$).

Iodic Acid ($HIO_3=176$).

Preparation.—(1.) By the action of chlorine on iodine suspended in water (Liebig)—

I_2	+	$5Cl_2$	+	$6H_2O$	=	$10HCl$	+	$2HIO_3$.
Iodine	+	Chlorine	+	Water	=	Hydrochloric acid	+	Iodic acid.

(2.) By boiling together strong nitric acid (10 parts) and iodine (1 part). The solution is afterwards evaporated to dryness and heated to 392 F° (200° C.), a white powder of I_2O_5 being thus obtained ($3I_2+10HNO_3=6HIO_3+10NO+2H_2O$).

(3.) By the action of dilute sulphuric acid on baric iodate. The crystals separate on the evaporation of the clear liquid ($Ba(IO_3)_2 + H_2SO_4 = 2HIO_3 + BaSO_4$)

Properties.—(α.) *Physical.*—Iodic acid is a white solid, having a sour taste, crystallizing in hexagonal tables ($I_2O_5,H_2O:Aq$) which are very soluble in water, but insoluble in alcohol. Specific gravity 4·629 at 0° C. Heated to 266° F. (130° C.), or treated with absolute alcohol, the crystals lose water and become HIO_3, which when heated to 338°F. (170° C.) leaves I_2O_5.

(β.) *Chemical.*—The acid first reddens and afterwards bleaches litmus. It is very much more stable than chloric acid. It slowly oxidizes most bodies. Deflagration occurs when organic matter, phosphorus or sulphur are heated with it. It does not blue starch, until acted on with reducing agents, such as SO_2, or H_2S, etc.; or by hydriodic acid, nitrous acid, phosphorous acid, etc., when it is decomposed, iodine being set free ($HIO_3 + 5HI = 3H_2O + 3I_2$), which will then form the blue iodide of starch.

Iodic acid is a monobasic acid, and forms iodates. (*See* IODATES.)

Periodic Acid ($HIO_4 = 192$).

History.—Discovered by Magnus.

Preparation.—In the process for the preparation of periodic acid there are several distinct steps to be noted :—

(α.) Chlorine is first passed through a solution of sodic iodate containing free soda, a sodic periodate being formed :—

$$2NaIO_3 + 6NaHO + 2Cl_2 = 4NaCl + Na_4I_2O_9 + 3H_2O.$$

Sodic iodate + Sodic hydrate + Chlorine = Sodic chloride + Sodic periodate (basic) + Water.

(β.) The insoluble sodic periodate formed is collected and treated with argentic nitrate :—

$$Na_4I_2O_9 + 4AgNO_3 = 4NaNO_3 + Ag_4I_2O_9.$$

Sodic periodate (basic) + Argentic nitrate = Sodic nitrate + Argentic periodate (basic).

(γ.) The basic argentic periodate formed is then dissolved in nitric acid, when a neutral argentic periodate is obtained.

$$Ag_4I_2O_9 + 2HNO_3 = 2AgIO_4 + AgNO_3 + H_2O.$$

Argentic periodate (basic) + Nitric acid = Argentic periodate (neutral) + Argentic nitrate + Water.

(δ.) This neutral argentic periodate is now boiled in water, when periodic acid and basic argentic periodate are formed.

$$4AgIO_4 + H_2O = 2(AgIO_4), Ag_2O + 2HIO_4.$$

Argentic periodate (neutral) + Water = Argentic periodate (basic) + Periodic acid.

It may also be prepared by decomposing plumbic periodate with sulphuric acid ($Pb(IO_4)_2 + H_2SO_4 = PbSO_4 + 2HIO_4$); or by adding iodine to an aqueous solution of perchloric acid ($2HClO_4 + I_2 = 2HIO_4 + Cl_2$).

Properties.—Periodic acid is a crystalline solid, melting at 271·4° F. (133° C.), very soluble in alcohol, ether, and water. The aqueous solution has a strong acid reaction. It may be boiled, but at 284° F. (140° C.) it is decomposed into I_2O_5, water and oxygen.

COMPOUNDS OF IODINE AND CHLORINE.

1.	Monochloride of Iodine	ICl.
2.	Trichloride of Iodine	ICl_3.
3.	Tetrachloride of Iodine	ICl_4.
4.	Pentachloride of Iodine	ICl_5. (?)

Monochloride of Iodine ($ICl = 161·9$) may be obtained directly, or by dissolving the product formed on boiling iodine with aqua regia, in ether, or by heating a mixture of iodine and potassic chlorate (Berzelius), ($I_2 + 3KClO_3 = KClO_4 + KIO_3 + KCl + O_2 + ICl$).

It is a dark, red, oily liquid, bleaching indigo, but not colouring starch. It solidifies on standing. The crystals are very deliquescent, and are decomposed by water ($5ICl + 3H_2O = HIO_3 + 5HCl + 2I_2$). They melt at 77° F. (24·7° C.), and boil at 213·8° F. (101° C.).

Trichloride of Iodine (ICl_3) is prepared either by direct combination, using a large excess of chlorine, or by heating I_2O_5 with hydrochloric acid ($I_2O_5 + 10HCl = 2Cl_2 + 5H_2O + 2ICl_3$).

It is a solid crystalline body, of a lemon yellow colour, melting at 77° F. (25° C.). It has no action on starch. When heated it gives off chlorine. In an atmosphere of chlorine it does not decompose at a temperature below 152·6° F. (67° C.), when ICl and free chlorine are formed, the ICl_3 being reformed on cooling.

Both these chlorides (ICl and ICl_3) are soluble in alcohol and ether, and are decomposed by potassic hydrate ($6KHO + 5ICl = 5KCl + KIO_3 + 2I_2 + 3H_2O$).

Tetrachloride of Iodine (ICl_4) is supposed to be formed when the monochloride is decomposed ($8ICl = 2ICl_4 + 3I_2$).

Pentachloride of Iodine (ICl_5) is also supposed to exist.

Iodine is believed to combine with bromine, forming IBr and IBr_5, these compounds having similar properties to the corresponding chlorides.

GENERALISATION ON THE HALOGENS (*that is, bodies forming salts, like common salt*), OR SALT RADICALS (*so called from their forming salts by direct contact with the metals*), CHIEFLY WITH REFERENCE TO CHLORINE, BROMINE, AND IODINE.

(1.) None of these bodies are found in nature in a free state. Where one is present, all are usually present; as, *e.g.*, in sea water, in mineral springs, in marine plants, in marine animals, etc.

(2.) They are all monad elements, one volume of the haloid element combining with one volume of hydrogen, to form two volumes of gaseous hydric acid, as HCl, HBr, HI, HF, all of which acids are closely allied in properties and reactions.

(3.) They all attack organic bodies, replacing and displacing hydrogen.

(4.) They all decompose water, forming compounds with the hydrogen, and setting free ozonic oxygen.

(5.) They all bleach, oxidize, and disinfect, by reason of their action on water (4).

(6.) They all act energetically on the metals, forming typical salts, which are very comparable as mono-, sesqui-, and per-salts.

(7.) They exhibit a remarkable sequence of properties :—

(α.) *Form and color.*	Chlorine is a yellow gas. Bromine is a red liquid, boiling at 145·4° F. Iodine is a black solid, boiling at 347° F.

(β.) *Specific gravity.*	Chlorine, 2·47. Bromine, 5·54. Iodine, 8·72.

(γ.) *Atomic weights.*	Chlorine, 35·5. Bromine, 80·0. Iodine, 127·0.

[NOTE.—The intensity of affinity seems to decrease, as the combining number increases.]

(δ.) *Compounds with hydrogen.*	Compounds of H and Cl, very stable. " H and Br, less stable. " H and I, less stable than HBr. " H and F, somewhat unstable.

(ε.) The reactions of the salts of the metals also exhibit a peculiar sequence :—

Fluoride of silver, very soluble in water.
Chloride of silver, insoluble in water, soluble in ammonia.
Bromide of silver " " slightly soluble in ammonia.
Iodide of silver " " insoluble in ammonia.

(ζ.) *The oxy-compounds.*
Compounds of O and F, non-existent.
,, O and Cl, very unstable.
,, O and Br, less unstable.
,, O and I, stable.

[Note.—The stability of the oxygen compounds is in inverse order to the stability of the hydrogen compounds.]

(η.) Their nitrogen compounds are all explosive.

(θ.) Chlorine is the most electro-negative of the haloids, and displaces bromine from its compounds; bromine stands next, and displaces iodine; nevertheless, in oxy-compounds, iodine will displace chlorine.

CHAPTER VI.

NITROGEN.

NITROGEN: — Atmospheric Air — Its Constituents — Compounds of Nitrogen and Oxygen—Nitrous oxide—Hyponitrous acid—Nitric oxide—Nitrous anhydride—Nitrous acid—Nitric peroxide—Nitric anhydride—Nitric acid—Compounds of Nitrogen and the Haloids — Compounds of Nitrogen with Oxygen and the Haloids.

NITROGEN (N).

Atomic Weight, 14 (*more exactly* 14·01). *Molecular Weight*, 28. *Molecular volume* $\boxed{}\boxed{}$. *Atomicity — Pentad* (^{v}), $N^{v}H_4Cl$; *Triad* ($'''$), $N'''H_3$; *Monad* ($'$), N_2O. *Specific gravity observed*, 0·9713, *calculated* $(0·0693 \times 14) = 0·9702$. 1 *litre weighs* 14 *criths* $(0·0896 \times 14) = 1·254$ *grm. at* 0° *C. and* 760 *mm.* 100 *cubic inches weigh* 30·002 *grns. at* 60° *F. and* 30 *B.P.*

Synonyms.—*Azote* (Lavoisier); *Nitrogen* (Chaptal).

History.—It was long ago noticed that a combustible body in burning vitiated the air. The Stahlians believed this vitiation to be due to the liberated "phlogiston." Hence they termed an air so vitiated "phlogisticated air." Dr. Rutherford (1772) of Edinburgh, struck by the change produced in atmospheric air by respiration, suggested that it was not an element, but a compound of two gases, and that in the act of breathing one of these gases was abstracted. Scheele and Lavoisier (1777) independently proved that air was a mixture of the newly discovered oxygen with another gas which Lavoisier termed *azote* (α and ζωή). This azote, Chaptal (1789) recognised as a constituent of nitre and nitric acid, and he, therefore, named it nitrogen.

Natural History.—(α.) In the *mineral kingdom*, nitrogen is found in a free state in the air to the extent of about 79 per cent. by volume, also in gaseous volcanic emanations, etc. It is found in combination (1) with oxygen and bases in nitres, and (2) with hydrogen, as ammonia, in air and water. (β.) In the *vegetable kingdom* it is present in small quantities in combination in most of the products of plant life, such as vegetable albumen, the various alkaloids, etc., whilst (γ,) in the *animal kingdom* it is found in all the fluids and tissues of the body, and plays an important part in the phenomena of life.

Nitrogen present in various Animal Substances.

	Per cent. by weight of Nitrogen.		Per cent. by weight of Nitrogen.
Cartilage	15·0	Gluten	16·0
Fibrin	15·4	Legumin	16·0 to 18·0
Albumen	15·5	Gelatin	18·3
Casein	15·7		
Urea (CH_4N_2O)	46·7	Sarcosin ($C_3H_7NO_2$)	15·7
Kreatin ($C_4H_9N_3O_2$)	32·1	Leucine ($C_6H_{13}NO_2$)	12·2
Kreatinin ($C_4H_7N_3O$)	37·1	Tyrosin ($C_9H_{11}NO_3$)	7·7

Preparation.—(1.) *By abstracting oxygen from atmospheric air* by one or other of the following methods:—

(*a*.) By the active combustion of phosphorus.
(*β*.) By the slow combustion of phosphorus in moist air.
(*γ*.) By the action of moist iron or certain other metallic filings.
(*δ*.) By the action of moistened alkaline sulphides.
(*ε*.) By the action of potassic pyrogallate.
(*ζ*.) By admixture with nitric oxide (NO) and subsequent washing.

(*η*.) By passing air (purified from CO_2 by caustic potash, and from moisture by sulphuric acid) over red hot iron or copper turnings, or, best of all, over finely divided copper reduced by hydrogen from the powdered oxide ($Cu_2 + [4N_2 + O_2]$ *air* $= 2CuO + 4N_2$).

(2.) *By the decomposition of ammonia or of its salts* by such methods as the following:—

(*a*.) By passing chlorine through an excess of ammonia solution. (If there be not an excess of ammonia, nitrogen chloride may be formed)—

$$\begin{array}{ccccccc} 8NH_3 & + & 3Cl_2 & = & 6NH_4Cl & + & N_2. \\ \text{Ammonia} & + & \text{Chlorine} & = & \text{Ammonic chloride} & + & \text{Nitrogen.} \end{array}$$

(*β*.) By heating ammonic nitrite—

$$\begin{array}{ccccc} NH_4NO_2 & = & 2H_2O & + & N_2. \\ \text{Ammonic nitrite} & = & \text{Water} & + & \text{Nitrogen.} \end{array}$$

(*γ*.) By heating together ammonic chloride and potassic nitrite—

$$\begin{array}{ccccccccc} KNO_2 & + & NH_4Cl & = & KCl & + & 2H_2O & + & N_2. \\ \text{Potassic nitrite} & + & \text{Ammonic chloride} & = & \text{Potassic chloride} & + & \text{Water} & + & \text{Nitrogen.} \end{array}$$

(*δ*.) By heating together solutions of ammonic chloride and ammonic nitrate (Maumené's process for preparing chlorine; see page 90).

[The chlorine produced may be removed by washing the products with an alkali.]

(ε.) By heating either ammonic bichromate alone [$(NH_4)_2\ Cr_2O_7$], or a mixture of ammonic chloride and potassic dichromate—

$$\underset{\text{Potassic dichromate}}{K_2Cr_2O_7} \;+\; \underset{\text{Ammonic chloride}}{2NH_4Cl} = \underset{\text{Chromic oxide}}{Cr_2O_3} \;+\; \underset{\text{Water}}{4H_2O} \;+\; \underset{\text{Potassic chloride}}{2KCl} \;+\; \underset{\text{Nitrogen.}}{N_2.}$$

Properties.—(α.) *Sensible.*—A colorless gas, without odor or taste.

(β.) *Physiological.*—It is not a poison (for we breathe it freely), but it will not support life. In the air it serves the purpose of a diluent, thereby rendering the oxygen less stimulating.

(γ.) *Physical.*—Its specific gravity is 0·9713. It is, therefore, a little lighter than air; 100 cubic inches weigh 30·119 grains (by calculation 30·002 grains), and 1 litre, at 0° C., 1·254 grms.

Nitrogen may be liquefied by cold and pressure. It is very slightly soluble in water—100 vols. absorb at 32° F. (0° C.), 2·03 vols.; and at 60° F. (15° C.) 1·48 vols. (Bunsen). It is more soluble in alcohol than in water.

It gives two characteristic spectra, the one obtained by passing the ordinary induction spark, and the other by a Leyden jar spark through a highly rarefied nitrogen tube.

(δ.) *Chemical.*—The chemical properties of nitrogen are remarkable for their negative character. It has no action on litmus or turmeric; it neither burns nor allows a taper to burn in it. It does not whiten lime water. Upon *oxygen* it is without action under ordinary conditions, but if sparks be transmitted through a mixture of oxygen and nitrogen, or if nitrogen mixed with hydrogen or if ammonia gas be burnt in an atmosphere of oxygen, nitric acid is formed.

Upon *chlorine and the haloids* it has no action, unless nascent, when explosive compounds result. [*Memo.* Being so feebly adapted for combination, many of its compounds are explosive.]

Upon *phosphorus, sulphur, selenium*, etc., it has no action. In the case of carbon, it forms, at a red heat and in the presence of an alkali or an alkaline earth, a metallic cyanide ($M'CN$).

It is said to combine directly with *boron* and *silicon.*

Upon *hydrogen* it has no action, unless the hydrogen be nascent, when ammonia is formed.

Upon the *metals* it has little action generally. In the case of tungsten, titanium, magnesium, and tantalum, all of which burn in it when heated, metallic nitrides are formed. Certain other nitrides are known, of which Mg_3N, Hg''_3N_2, Cu_6N_2, and CrN are illustrations.

It has no action on *organic bodies.*

Tests.—In its free state we know it by its negative characters. In combination either as nitric acid or as ammonia it may be recognised by the special tests for these bodies.

In *organic compounds* we estimate it quantitatively from the amount of ammonia formed when the organic matter is combusted with soda-lime. If the nitrogen be present in the body as an oxide, it must then be determined as free nitrogen by processes to be hereafter described. (*See* ORGANIC ANALYSIS.)

Uses.—These are confined to Nature as a diluent in the air, and as a constituent of tissues.

ATMOSPHERIC AIR (ἀτμός vapor, and σφαίρα a sphere).

History.—(α.) *Ancient opinions.*—The air was originally regarded as an element. The ancient chemists made no distinction between the various aëriform bodies, calling them all *air*, and this *common air*. In 1640, Van Helmont observed differences in air, and he adopted the word *gas* or *gaz*, to distinguish them (thus gas-pinque, gas-siccum, gas-fatiginosum, gas silvestre.—De Flatibus.) In 1650, Macquer popularised the word *gas*, and distinguished a gas from a vapor. In 1660 Boyle suspected a difference in the composition of different gases from noting differences in their combustibility, etc.

(β.) *Modern opinions.*—In 1772, Rutherford discovered nitrogen, and in 1774, Priestley discovered oxygen. In 1777, Lavoisier proved that air consisted of a mixture of these two gases, in the proportion of 1 volume of oxygen and 4 volumes of nitrogen. His experiment in proof consisted in boiling mercury for several days in a given bulk of air, noting the loss, the quantity of the calx of mercury formed (HgO), and the quantity of oxygen produced on heating a given weight of the calx. About the same time Scheele and Priestley independently arrived at similar conclusions, the former absorbing the oxygen with potassic sulphide, and the latter with nitric oxide. More careful experiments were afterwards conducted by Cavendish (1781), Prout, Biot and Arago, Dumas and Boussingault, Regnault and others.

Properties.—(α.) *Physical.*—The *specific gravity* of air is regarded as 1; that is, it is regarded at 0° C. and at 30 Bar. Pr. (760 mm.) as the unit and standard of comparison for gases and vapors. Its density is directly proportional to the pressure (Boyle's law). Thus the density decreases in a geometric ratio to the increase of the height of the air above the sea level.

Weight of the Air.

100 cubic inches weigh	(Prout)	31·117	grains.
,, ,, ,, ,,	(Biot and Arago)	31·074	,,
,, ,, ,, ,,	(Dumas and Boussingault)	31·086	,,
,, ,, ,, ,,	(Regnault at Paris latitude) ..	30·935	,,
,, ,, ,, ,,	(Mean of the four observations) ..	31·053	,,

Taking the mean of these experiments, 1 litre of air weighs at 0° C. and 760 mm., 1·2936 grm., and 1 cubic foot, 536·6 grains. Air is therefore 14·45 times heavier than hydrogen, 816 times lighter than water, and 10,500 times lighter than mercury.

The *average pressure* of the air on the surface of the earth, and at the level of the ocean is equal, on an average, to 15 lbs. on the square inch (more accurately 1033·3 grms. on 1 square centimeter of surface at the sea's level, or 27,000,000 tons on every square mile), that is, the air is capable of supporting a column of mercury of 30 inches or 760 mm. at 0° C., or a column of water of 34 feet. Pressure, however, is not constant, owing to variations in temperature, solar radiation, etc.; hence in gas determinations, it is always necessary to correct for the pressure of air. As we ascend, the pressure diminishes with the density, it being halved for every 3·4 miles. It follows, therefore, that whatever may be the extent of the air (estimated at from 40 to 45 miles), one-half of the atmosphere must be confined to about 3·5 miles of the earth. But the temperature at different places varies, owing to the unequal heating effect of the sun on different portions of the earth's surface. Hence arise "winds," *i.e.*, motions of the atmosphere. What are called "breezes" are dependent on mere limited alterations, whilst "trade winds" depend on differences of air temperature in the Equatorial zones and Polar regions.

The *average temperature* of the air in England is 60° F. (15·56° C.). But this varies at different heights, the temperature decreasing 1° F. for every 300 feet, or 1° C. for every 550 feet.

The warmth of the air is mainly due to radiation from the earth's surface. The luminous rays from the sun do not heat the air in their passage through it. The heat rays are partly absorbed, and supply some of the atmospheric warmth. The visible rays (together with those heat rays not previously absorbed) reach the earth, and are converted into heat, which, radiating from the earth, are then absorbed by the aqueous vapors of the air. Thus the luminous rays pass from the sun through the aqueous vapors of the air to heat the earth, but the dark heat rays radiating from the earth are entrapped by the aqueous vapors of the air, thereby heating the air. By the constant rise of the heated air and the constant fall of the colder air, the atmosphere is kept uniformly heated.

The *line of perpetual snow*, that is, the height at which the mean temperature of the air does not rise above the freezing point (which varies for different latitudes, and even at the same latitude is affected by local causes), is in this country about 6,000 feet, whilst in the tropics under the equator it is 15,200 ft., and at latitude 75° is at the sea level.

Air is a *refractor of light*;—hence the existence of twilight.

(β.) *Chemical.*—Air is a *mechanical mixture* of nitrogen, oxygen and other gases, as proved by the following circumstances:—

(*a.*) On mixing oxygen and nitrogen in their proper aerial proportions, neither change of volume, nor heat, nor electricity results.

(*b.*) The relative amounts of oxygen and nitrogen present in the air are not their combining weights, nor any multiple thereof.

(*c.*) When air is shaken up with fresh boiled water, the gases dissolve in their normal proportion, *i.e.*, as 1 of nitrogen to 1·87 of oxygen; and not in the proportion in which they are contained in air, viz., as 4 of nitrogen to 1 of oxygen.

Air also contains certain finely divided solids in suspension, such as sodic chloride, sporules, volcanic dust, etc.

Composition.

General average Analysis of Air.

	Oxygen	20·61
	Nitrogen	77·95
	Carbonic anhydride	·04
	Aqueous vapour	1·40
	Nitric acid	traces.
	Ammonia	
	Carburetted hydrogen	
and in towns	Sulphuretted hydrogen	traces.
	Sulphurous anhydride	

Constituents of the Air.

(1.) *Oxygen and Nitrogen.*—The proportion of these gases respectively present in air was, first of all, determined by Cavendish in 1781 (*Phil. Trans.*, 1783, p. 106). Analyses may be conducted in various ways:—

(A.) *By reagents which absorb the oxygen at ordinary temperatures and leave the nitrogen, as follows:—*

(*a.*) By mixing a given bulk of air with a given bulk of nitric oxide (NO) in a graduated tube standing over water. The oxygen present in the air combines with the nitric oxide (NO) to form nitric peroxide (N_2O_4), which is dissolved as soon as formed by the water in the tube.

Example.—Suppose that to 5 volumes of air we add 5 volumes of NO, we should find that 3 volumes would be immediately absorbed by the water, leaving only 7 volumes in the tube. Of every 3 volumes of N_2O_4 so absorbed, 1 volume we know to be oxygen. It follows, therefore, that 1 volume of the 5 volumes of the original air was oxygen.

There are many sources of error in this process. The NO may contain N_2O, whilst N_2O_3 may be formed in variable proportion, as well as N_2O_4. This process of analysis, therefore, although considerably improved by Falconer, Fontana, Cavendish, Humboldt, Gay Lussac, Thénard, and others, is wanting in accuracy.

(β.) By exposing a given volume of air to the action of an alkaline sulphide. (Scheele; improved by De Marti.)

(γ.) By exposing a given volume of air to the action of moist lead. (Saussure.)

(δ.) By exposing a given volume of air to the action of sheet copper and dilute sulphuric acid. (Gay Lussac.)

(ϵ.) By introducing a piece of phosphorus into a given volume of air standing over water. (Berthollet and Parrot, Achard, Brunner, Reboul, etc.)

(ζ.) By a solution of nitric oxide in ferrous sulphate ($4FeSO_4 + 2NO$), a brown liquid being formed which rapidly absorbs oxygen. (Sir H. Davy.)

(η.) Either by an ammoniacal solution of cuprous sulphate, prepared by passing SO_2 through an ammoniacal solution of $CuSO_4$, and dissolving the precipitate formed in ammonia; or by a solution of cuprous oxide (Cu_2O) in ammonia. (Graham.)

(θ.) By a strong solution of pyrogallic acid ($C_{12}H_6O_6$) in caustic potash (potassic pyrogallate).

(B.) *By agents which absorb the oxygen at high temperatures and leave the nitrogen.*—A given volume of air is first passed, (1), over *calcic chloride*, then (2), over *caustic potash*, and finally (3), over *ignited copper* reduced from its oxide, severally contained in glass tubes accurately weighed before the experiment is commenced. The increase in the weight (1) of the *calcic chloride* tube indicates the moisture, (2) of the *caustic potash* tube, the *carbonic anhydride*, and (3) of the *copper* tubes the *oxygen* contained in the volume of air operated upon. The residual gas, which is nitrogen, may be collected in an exhausted and weighed globe, the increase in the weight of which after the experiment is complete gives the nitrogen. (Dumas and Boussingault, 1841. Vide *Ann. Chem. Phys.* [3], III., 257.)

(C.) *By exploding the air with hydrogen in a eudiometer.* (Regnault, Bunsen, Frankland, Williamson, Angus Smith, Russell, etc.)—Every 1 volume of oxygen requires 2 volumes of hydrogen to form 2 volumes of water gas (H_2O).

Experiment.—To 100 volumes of air from which the ammonia, moisture and carbonic acid have been removed, add 50 volumes of hydrogen, and explode. The 150 volumes will shrink (water being condensed) to 87 volumes;

$$150 - 87 = 63 \text{ volumes loss;}$$

Of these 63 volumes of H_2O condensed, one-third is oxygen;

Therefore, $\frac{63}{3} = 21$ volumes of oxygen in 100 volumes of air.

[MEMO.—We may here note, that conversely the quantity of hydrogen present in a mixed gas may be estimated by exploding the gas with *oxygen* and noting the loss, two-thirds of which is hydrogen.]

This combination of oxygen and hydrogen may be effected slowly by using pellets of spongy platinum.

Results of analysis.—Taking the average of numerous experiments, ordinary air may be regarded (disregarding other constituents) as a mechanical mixture of 79·15 volumes of nitrogen with 20·85 volumes of oxygen, or of 76·93 parts by weight of nitrogen with 23·07 parts of oxygen. The following results were obtained by Dumas and Boussingault and by Regnault:—

		Dumas and Boussingault.	Regnault.	Mean.	In round numbers.
By volume	Nitrogen ..	79·23	79·07	79·15	79
	Oxygen ..	20·77	20·93	20·85	21
		100·00	100·00	100·00	100
By weight	Nitrogen ..	76·995	76·87	76·93	77
	Oxygen ..	23·005	23·13	23·07	23
		100·000	100·00	100·00	100

The proportions of oxygen and nitrogen present in the air, have been found not to vary more than from 20·80 to 20·97 per cent. by volume. Angus Smith records the air of the Scotch moor as containing 20·999 per cent. by vol. of oxygen, of the town in foggy weather 20·82, of inhabited rooms and crowded theatres 20·28, and of mine air 20·26. This uniformity is dependent on the operation of winds and upon diffusion, by which gases mix in opposition to gravitation, and when mixed do not again separate.

(2.) *Ozone.*—The presence of ozone in the air has been abundantly proved. It is produced by electrical discharges as well as during the evaporation of water. It may be detected by test papers. (See page 75.) The general facts relating to atmospheric ozone may be stated as follows, although it must be admitted that our knowledge on the subject lacks certainty:—

1. More ozone is present during the night than during the day, whilst most of all is found at day-break.
2. More is found in winter than in summer, and least in autumn.
3. More is found at high than at low levels.
4. More is found on the sea coast, and specially when the wind is blowing from the sea, than inland.
5. More is found in the country than in towns, owing to the presence in the latter of SO_2 and organic emanations.
6. More is found after a thunderstorm than at any other time; least of all is found on damp foggy days.
7. More is found with western than with eastern winds.

8. The maximum quantity of ozone in the air, never exceeds $\frac{1}{700000}$ part its bulk (Houzeau). Its chief source is atmospheric electricity, and as minor sources the action of aromatic plants and flowers, etc. (See Glaisher's remarks in Appendix to Cholera Reports of Board of Health, 1855, pp. 71—73, 89, 90.)

(3.) *Aqueous vapor.*—The maximum quantity to be found in air (saturation) is constant for temperature but independent of pressure. Quantity is determined by instruments called *hygrometers* (ὑγρὸς, moisture, and μέτρον, a measure), hygroscopes, or psychrometers (ψῦχρος, cold). A large number of common things, such as seaweeds, catgut, whipcord, etc., are hygroscopic, and are consequently used as weather instruments.

On cooling a non-saturated air, a temperature is reached when for that temperature the air will be saturated, and below which a separation of the moisture as dew or mist occurs. This is called *the dew point.* The dew point varies according to the quantity of moisture present in the original air, by determining which the amount of moisture present in unsaturated air may be estimated.

Daniel's hygrometer, the action of which depends on cooling the air by the evaporation of ether until moisture begins to be deposited, and *Mason's wet and dry bulb thermometers,* are the common instruments in use for measuring the hygroscopicity of the air. The actual amount of moisture in the air may be estimated, by passing a given volume of air through a weighed tube containing calcic chloride, the increase in the weight of the tube after the experiment indicating the amount of moisture present in the volume of air operated upon.

Russell ("On the Impurities in London Air," by W. J. Russell, Ph.D., F.R.S., in the Monthly Weather Report of the Meteorological Office, August, 1885) records the following as the mean of 23 analyses of dew :—

Results given in grams per Litre.

Sulphuric Acid	0·0382
Hydrochloric Acid	0·0188
Ammonia	0·0079
Oxygen required to Oxidize	0·0282

Russell considers that the composition of dew and of rain (analysis showing a close similarity in their several constituents) may be considered as indications of the purity of an air. The results given in the report are interesting.

General facts respecting moisture.—(*a.*) Air rarely contains its full saturated amount of moisture, except in very cold weather or in very hot tropical seas ; in such cases the air becomes very oppressive.

(*b.*) If the air were saturated with moisture, the amount present would be as follows :—

Amounts of Aqueous Vapor in 1,000 *volumes of Air when saturated.*

Tempt. Fahr. (degrees).	1000 vols. of dry air become when saturated (volumes).	1000 vols. of saturated air contain aq. vap. (volumes).	One cubic foot of air saturated (B.P.30 in.)		
			Contains aq. vap. (cubic inches).	Contains aq. vap. (grains).	And it weighs (grains).
10	1002·3	1·12	1·9354	0·84	592·94
20	1003·6	2·29	3·9571	1·30	580·26
30	1005·6	5·57	9·6250	1·97	567·99
40	1008·3	8·23	14·2214	2·86	556·03
50	1012·0	11·76	20·3213	4·10	544·36
60	1017·3	17·06	29·4797	5·77	532·84
70	1024·4	23·82	41·1610	8·01	521·41
80	1034·1	32·98	56·9890	10·98	509·97
90	1047·0	43·93	75·9110	14·85	498·43
100	1063·9	60·07	103·8010	19·84	486·65

(*c.*) The most comfortable degree of saturation is from 66 to 70 per cent. More than this checks evaporation from the body, whilst less causes too great evaporation, thereby parching the mouth and drying the skin.

(*d.*) It has been noted that in certain places, remarkable as health resorts, the degree of saturation is singularly uniform.

(4.) *Carbonic acid.*—This is always present in air. It may be estimated in different ways as follows :

(*α.*) By passing a given volume of air through a weighed tube containing caustic potash. The aqueous vapor must first be got rid of by passing the air over chloride of calcium. The increase in the weight of the tube containing the caustic potash, indicates the amount of carbonic acid present.

(*β.*) By shaking up a gallon bottle of the air to be examined, with a known quantity of lime water. The quantity of the lime remaining unneutralized must then be determined by a standard solution of oxalic acid. (Pettenkofer.)

(*γ.*) By noting the degree of turbidity produced when a given volume of air is passed through a given bulk either of lime or of baryta water.

(*δ.*) By shaking up half an ounce of baryta water (consisting of one half of a cold saturated solution and one-half water) with different bulks of the air under examination. The least turbidity indicates—

With 23 ozs. of air	.. .. ..	0·04 CO_2 per cent.
9 ,,	.. .. ..	0·10 ,,
5 ,,	.. .. ..	0·20 ,,
3½ ,,	.. .. ..	0·30 ,,
2¾ ,,	.. .. ..	0·40 ,,
2 ,,	.. .. ..	0·60 ,,
1½ ,,	.. .. ..	0·90 ,,

General facts relating to carbonic acid in the air.—(*a.*) A normal atmosphere contains 4·5 volumes of CO_2 in 10,000 of air (*i.e.*, 0·04 to 0·05 per cent.).

(*b.*) The proportion of carbonic acid is greater at high than at low altitudes. (Frankland.)

Chamounix ...	3,000 feet,	6·3 parts of CO_2 per 10,000.
Grand Mulets...	11,000 ,,	11·1 ,, ,,

(*c.*) The proportion varies with the weather, the quantity being greatest in foggy weather and least in fine weather.

The following results were obtained by Russell :—

Results stated in grams per 1,000 *cubic feet of air.*

	Mean of Experiments.	Sulphuric Acid.	Hydrochloric Acid.	Carbonic Acid.
				Vols. in 10,000.
In fine weather	12	0·0128	0·0010	3·78
In dull weather	11	0·0319	0·0036	4·50
In foggy weather	4	0·0460	0·0028	5·10

(*d.*) The proportion is slightly greater on the surface of the ocean by day than inland (from the action of the sun on the water?). Lewy found 4·7 parts per 10,000 in the air at the middle of the Atlantic.

(*e.*) The proportion of carbonic anhydride present in the air varies greatly.

Proportions of Carbonic Acid per 10,000 *parts of Air.*

	Extremes.	Average.
In cities and towns :—		
London	2·8—4·3	3·4
Manchester	4·9—15	5·4
Munich		5·0
Madrid	3·0—8·0	5·2
Paris	3·6—5·1	4·9
In dwelling-houses :—		
By day (large rooms)	5·4—8·7	6·8
,, (small rooms)		12·7
By night (common rooms)		13·4
,, (bed rooms)	28—50	36·0
In schools :—		
By day, English	9·7—31	21·5
,, French	27—47	24·7
,, German		39·2
In mills and workshops	28—30	29·1
Places of public resort :—		
London law courts	4·8—19·8	12·3
London theatres	7·6—32·0	14·9
Manchester theatres	10·2—27·3	14·8
Paris theatres	23—43	33·0

(*f.*) Expired air contains from 350 to 500 parts per 10,000, or an average of 425 parts in 10,000 of air.

(*g.*) Roscoe states that the air in rooms never contains more than 0·5 per cent., or 50 parts in 10,000, owing to diffusion and to the porous nature of the walls.

(*h.*) When a chafing dish was lighted and left to burn until the carbonic acid generated was sufficient to extinguish the fire, the proportion of CO_2 was found to be 14 per cent. or 1,400 parts per 10,000 of air.

(*i.*) Here it will be well to note the vitiating effects on air of different kinds of fuel and illuminating agents.

Carbonic Acid produced and Air vitiated per hour.

	Carbonic acid produced (cubic inches).	Air vitiated and used (cubic feet).
A man	1,201	723
A horse or cow	14,750	8,591
Batswing burner (3 feet per hour cannel gas)	4,304	2,513
Fishtail or Argand (5 ,, ,, common gas)	4,752	2,779
Moderator lamp, consuming 643 grains oil per hour	3,857	2,410
Paraffin ,, ,, 400 ,, ,,	2,666	1,658
,, candle ,, 120 ,, ,,	800	498
Spermaceti candle ,, 130 ,, ,,	809	502
Composite ,, ,, 140 ,, ,,	829	515
Wax ,, ,, 168 ,, ,,	1,062	670
Tallow ,, ,, 143 ,, ,,	858	529

(*j.*) Lastly, we may note that the quantity, according to Pettenkofer, which marks the boundary line between pure and impure air is 0·1 per cent. If, therefore, we find more than 10 parts of CO_2 in 10,000 parts of air, we should be justified in regarding that atmosphere as dangerously polluted.

(5.) *Ammonia.*—Free and saline ammonia is generally present in the air in small quantities. This was first observed by Liebig. It may be estimated by passing a known volume of air through a known quantity of dilute sulphuric acid, contained in a tube filled with glass beads. The amount of acid left unsaturated must be afterwards determined.

Proportions of ammonia (NH_3) *found in* 1 *million parts of air.*

Fresenius (by day)	0·098
,, (by night)	0·169
Groeger	0·383
Kemp	3·880
Letheby and Tidy	from 4·101 to 6·203

(Vide *Quarterly Journal of Agriculture*, 1849, *p.* 160.)

Ammonia is always more abundant in the air in dry than in wet weather, in town than in country, and in summer than in winter.

Proportions of Ammonia found in 1 million parts of Rain Water.

	Parts per million.
Boussingault (Liebfrauenberg)	0·80
Lawes and Gilbert (Rothamstead)	1·00
Russell	2·80
Barral and Boussingault (Paris)	3 to 4
Letheby and Tidy (London Hospital)	4 to 6

(6.) *Nitric acid and other oxides of nitrogen.*—Nitric acid is always present in small quantities in the atmosphere, but specially during a thunderstorm, electrical discharges determining the union of the nitrogen and oxygen. Its presence may also be due to the action of ozone on atmospheric ammonia. The acid is present in rain water to the extent, at times, according to Messrs. Lawes and Gilbert, of 3·71 parts in a million.

Probably ammonia and nitric acid are the sources from which plants derive their nitrogen, vegetation being apparently unable to assimilate the gas when presented to it in a free state.

(7.) *Sulphurous and sulphuric acids.*—These are always present in the atmosphere of towns where coal is burnt, and may often be seen upon our windows in the form of ammonic sulphate. In certain localities where sulphur is burnt or metals refined, a large escape of sulphurous acid into the air is not uncommon. The rain from the roof of the London Hospital College was found to contain from 0·942 grain to 4·357 grains of sulphuric acid (H_2SO_4) per gallon. (*See* Table, p. 125).

(8.) *Organic and suspended matters, etc.*—Certain organic vapors, floating particles, germs of fungi, etc., are found in the air, and are revealed by every sunbeam, owing to their property of reflecting light. That such organic particles are present, the development of mould and of infusoria in organic solutions abundantly testifies. Tyndall's researches have shown the power possessed by cotton wool in filtering off these solid particles. A mist or fog is due to the presence of minute liquid particles. Suspended solid particles are rapidly deposited by the electrification of air. (Lodge.)

Russell ("On the Impurities of London Air," August, 1885), has made very numerous estimations of the organic matter in the air, and has found a close relationship between the weather and the quantity of organic matter present. The following mean numbers were obtained:—

ORGANIC MATTER IN AIR.

(*Grams per* 1000 *cubic feet of Air.*)

	Organic Carbon.	Organic Nitrogen.
In fine weather	0·0033	0·0002
In dull weather	0·0101	0·0002
In foggy weather	0·0239	0·0005

(9.) *Saline matters.*—Certain finely divided salts, such as sodic chloride, etc., are found in the air, and especially in the immediate neighbourhood of the sea. Common salt, however, exists in small proportions in all air. Russell has estimated the chlorides in the air under different conditions. His results are stated in the table on page 125.

COMPOUNDS OF NITROGEN AND OXYGEN.

Nitrogen and oxygen have but little tendency to combine directly, nevertheless by indirect combination they form a very complete series of chemical compounds, which may be thus tabulated :—

The Oxides of Nitrogen.

Formula of Oxides.		Acids.	Formula of acids.
N_2O (Nitrous oxide)	$+ H_2O$	= Hyponitrous acid	(HNO)
N_2O_2 (NO) (Nitric oxide)	No acid		
N_2O_3 (Nitrous anhydride)	$+ H_2O$	= Nitrous acid	(HNO_2)
N_2O_4 (NO_2) (Nitric peroxide)	$+ H_2O$	= { Nitrous acid and Nitric acid	
N_2O_5 (Nitric anhydride)	$+ H_2O$	= Nitric acid	(HNO_3)

Nitrous Oxide (N_2O).

Molecular weight, 44. *Molecular volume,* ☐☐. *Relative weight* ($H=1$), 22. *Specific gravity observed,* 1·527, *calculated* ($0·0693 \times 22$) 1·5246. 1 *Litre weighs* ($0·0896 \times 22$) 1·971 *grms., and* 100 *cubic inches* 47·146 *grains.*

Synonyms.—*Dephlogisticated nitrous air* (Priestley); *nitrous oxide* and *laughing gas* (Davy); *protoxide of nitrogen*; *nitrogen monoxide*; *hyponitrous anhydride.*

History.—Discovered by Priestley (1772) when acting on nitric oxide with iron filings. Examined by the Dutch chemists (1793) and proved by them to be a compound of nitrogen and oxygen. Its physiological action was investigated by Davy (1809) at the Clifton Pulmonic Institution.

Preparation.—(1.) By the action of iron filings on nitric oxide (NO). (Priestley.)

(2.) By heating to 470° F. (243° C.) ammonium nitrate (or ammonium chloride and dilute nitric acid, Sp. Gr. 1·2, as suggested by L. Smith). (Berthollet and Davy.)

$$\underset{\text{Ammonium nitrate}}{NH_4,NO_3} = \underset{\text{Water}}{2H_2O} + \underset{\text{Nitrous oxide.}}{N_2O.}$$

N.B.—If the temperature applied be above 500° F. (260° C.) other changes occur nitric oxide and nitrogen being evolved, and a mixture of ammonic nitrite and nitrate subliming. If ammonic chloride be present, the N_2O will be mixed with chlorine (p. 90). The gas, therefore, should be passed through a solution of ferrous sulphate to absorb NO, and through caustic potash to free it from chlorine.

(3.) By the action of dilute nitric acid (Sp. Gr. 1·2) on granulated zinc. (Grotthus.)

$10HNO_3$	+	Zn_4	=	$4(Zn2NO_3)$	+	$5H_2O$	+	N_2O.
Nitric acid	+	Zinc	=	Zinc nitrate	+	Water	+	Nitrous oxide.

(4.) By decomposing nitric acid with a hydrochloric acid solution of stannous chloride.

(5.) By passing nitric oxide (NO) through a solution of sulphurous anhydride.

[When the gas is required for inhalation it should be purified by passing it first through a potash solution to get rid of acid vapors, and then through a ferrous sulphate solution to get rid of nitric oxide.]

Properties.—(α.) *Sensible.*—A sweet-tasted gas, without color or odor.

(β.) *Physiological.*—When breathed it induces transient intoxication, with strong muscular exertions and uncontrollable laughter (Laughing Gas). If the inhalation be continued it produces complete anæsthesia, brief as to time, and supposed harmless as regards its after effects. Liquid and solid nitrous oxide blister the skin when brought into contact with it. (Davy, Roget, Southey, Kingslake, Wedgwood, etc.)

(γ.) *Physical.*—In nitrous oxide 2 volumes of nitrogen and 1 volume of oxygen are condensed into 2 volumes. If 2 volumes of N_2O be heated to bright redness, it undergoes decomposition and permanently expands to 3 volumes. Thus its composition is determined :—

Nitrogen	$N_2 = 28$	vols. 2	=vols. 2.
Oxygen	$O = 16$	vol. 1	

It has a specific gravity of 1·524 (calculated 1·524) ; 100 cubic inches weigh 47·34 grains (or as calculated 47·146 grains), and 1 litre 1·971 grms. At a temperature of 0° C. and 30 atmospheres, or at 45° F. (7° C.) and 50 atmospheres pressure, it becomes a colourless liquid (Faraday, 1823), not miscible with water, having a specific gravity of 0·936 at 0° C., and boiling at —126° F. (—88° C.). It has the smallest refracting power of any known liquid (Faraday). When the liquid is exposed to the air, its evaporation is so rapid that it freezes itself, becoming a white flaky solid, which melts at —148° F. (—100° C.). The liquid may be solidified to colorless crystals by the cold produced by solid CO_2 and ether evaporated in vacuo. Liquid nitrous oxide has a high co-efficient of expansion, 1 volume at 0° C. becoming 1·1202 volumes at 20° C. If liquid nitrous oxide be dissolved in carbon disulphide and evaporated " in vacuo," a temperature of —220° F. (—140° C.) is produced. Nitrous oxide is decomposed either when heated in a porcelain tube or exposed to the action of electric sparks.

The gas is freely soluble in water ; 100 volumes of water at 32° F. (0° C.) absorb 130 volumes ; at 60° F. (15·5° C.) 78 volumes, and at 75° F. (24° C.) 60 volumes of the gas. It is more soluble in alcohol, ether, and the volatile oils, than it is in water.

(δ.) *Chemical.*—Nitrous oxide is a neutral body, without action on litmus or turmeric. It is not combustible, but supports combustion almost as powerfully as oxygen, provided the combustible body is burning freely. If the combustion be feeble, the temperature will be insufficient to decompose the gas, this being a necessary condition of rendering it a supporter of combustion. In fact combustion in nitrous oxide is combustion in oxygen.

Nitrous oxide may be known from oxygen as follows :—

(1.) It does not form red fumes with nitric oxide.

(2.) It is very much more soluble in water.

(3.) It is not absorbed by potassic pyrogallate.

(4.) If phosphorus or potassium be burnt in it, the volume of residual gas (nitrogen) is identical with that of the original gas ; for—

$$\boxed{N \mid N} + \boxed{O} = \boxed{N_2 \mid O}$$

whereas this is not the case when phosphorus or potassium is burnt in oxygen.

With hydrogen, nitrous oxide explodes volume for volume—

$$\boxed{N_2 \vdots O} + \boxed{H \vdots H} = \boxed{H_2 \vdots O} + \boxed{N \vdots N}$$

In this manner the composition of the gas may be proved, and its quantity in mixture estimated.

On the metals, nitrous oxide has no action in the cold, but zinc, iron, and the alkaline metals when heated, burn in it freely. It will be noted that the bulk of nitrogen remaining when combustion is complete will be equal to the bulk of the gas originally employed. If potassium or sodium be burnt in the gas the metals become oxidized, the peroxides so formed becoming nitrates, when more strongly heated in the gas.

Uses.—In *medicine* it is used as an anæsthetic. It is most important that the gas for this purpose should be rendered pure by being well washed in potassic hydrate and ferrous sulphate solutions.

In *the laboratory* the intense cold produced by the action of carbon disulphide on its solid or liquid form is valuable in research.

Hyponitrous Acid (HNO = 31).

This acid has never been isolated. If, however, an alkaline nitrate be treated with sodium amalgam, a nitrite is first formed ($NaNO_2$), which undergoes further reduction to the state of hyponitrite (NaNO):—

$NaNO_3$	+	$2H_2$	=	$NaNO$	+	$2H_2O$.
Sodium nitrate	+	Hydrogen	=	Sodium hyponitrite	+	Water.

On neutralizing the alkaline solution with acetic acid, and adding argentic nitrate, the yellow argentic hyponitrite ($AgNO$) is precipitated. The sodic hyponitrite solution, when heated with acetic acid, gives off nitrous oxide ($2HNO = N_2O + H_2O$). (Divers, Proc. Royal Society, 1871.)

Nitric Oxide (NO).

Molecular weight, 30. *Molecular volume* ☐☐, *Relative weight,* ($H = 1$), 15. *Specific gravity,* 1·039. 100 *cubic inches weigh* 32·145 *grs., and* 1 *litre* (0·0896 × 15) 1·344 *grms.*

Synonyms.—*Nitrous air* (Priestley); *Binoxide and Deutoxide of Nitrogen; Nitrogen Dioxide; Azotyl, Nitrosyl. Gas sylvestre* (Van Helmont).

Preparation.—(1.) By the action of dilute nitric acid (Sp. Gr. 1·2) on copper (with or without heat). [Other metals, such as lead, mercury, silver, bismuth, etc., and also phosphorus and other easily oxidizable bodies, may be used, but in these cases a stronger acid is required].

$3Cu$	+	$8HNO_3$	=	$3Cu(NO_3)_2$	+	$4H_2O$	+	$2NO$.
Copper	+	Nitric acid	=	Cupric nitrate	+	Water	+	Nitric oxide.

To obtain pure nitric oxide, pass the gas through a cold concentrated solution of ferrous sulphate. This absorbs it, forming $4FeSO_4, 2NO$. When this solution is heated, pure nitric oxide is evolved.

(2) By decomposing nitre with ferrous chloride or with ferrous sulphate in their respective acid solutions:—

(*a.*)	$6FeCl_2$	+	$8HCl$	+	$2KNO_3$	=	$3Fe_2Cl_6$	+	$4H_2O$	+	$2KCl$	+	$2NO$.
	Ferrous chloride	+	Hydrochloric acid	+	Potassic nitrate	=	Ferric chloride	+	Water	+	Potassic chloride	+	Nitric oxide.

3.)	$6FeSO_4$	+	$5H_2SO_4$	+	$2KNO_3$	=	$3(Fe_23SO_4)$	+	$2HKSO_4$	+	$4H_2O$	+	$2NO$
	Ferrous sulphate	+	Sulphuric acid	+	Potassic nitrate	=	Ferric sulphate	+	Hydric potassic sulphate	+	Water	+	Nitric oxide

(3.) By passing ammonia gas over heated manganese dioxide:—

$5MnO_2$	+	$2NH_3$	=	$5MnO$	+	$3H_2O$	+	$2NO$.
Manganese dioxide	+	Ammonia	=	Manganous oxide	+	Water	+	Nitric oxide.

Properties.—(*a.*) *Sensible and Physiological.* — A colorless gas, having a strong and disagreeable odor. It produces violent irritation when breathed (Davy). It destroys life if respired for more than a few seconds.

(*β.*) *Physical.*—Nitric oxide consists of equal volumes of nitrogen and oxygen united without condensation.

Its specific gravity, both by experiment and by calculation (15 × 0·0693), is 1·039. 100 cubic inches weigh 32·145 grains, and 1 litre 1·344 grms. It is the most stable of all the nitrogen oxides, and is consequently that oxide most commonly formed by the decomposition of other oxides. For neither a red heat (nor, indeed, any heat short of a white heat) nor electric sparks decompose it when the gas is quite dry, although in the presence of moisture both heat and electricity decompose it. 100 volumes of water dissolve 5 volumes of the gas, and 100 volumes of alcohol 27·4 volumes.

(γ.) *Chemical.*—The composition of nitric oxide is proved by heating potassium in a known volume of the gas over mercury. The residual gas will be found to be one-half the volume of the original gas, and to consist of pure nitrogen.

Provided no free oxygen be present, nitric oxide is neutral both to litmus and turmeric. It neither burns nor supports combustion, unless the combustible body, when introduced, be burning sufficiently energetically to effect its decomposition. Under such circumstances both carbon and phosphorus burn in it freely, the former leaving a mixture of nitrogen and carbonic anhydride, and the latter pure nitrogen, as the gaseous products of their combustion.

The special characteristic of nitric oxide is its affinity for oxygen. The red fumes of nitrous anhydride (N_2O_3) and nitric peroxide (N_2O_4), formed by its combination with oxygen, distinguish it from all other gases. The relative proportion of these two gases (N_2O_3 and N_2O_4) formed when nitric oxide is mixed with oxygen varies, and inasmuch as they have different solubilities, it is not possible to estimate the oxygen accurately in any mixture by this means. Nitric oxide has no action on hydrogen at ordinary temperatures. A mixture of equal volumes of hydrogen and nitric oxide burns with a green flame, whereas the mixture in like proportion of hydrogen and nitrous oxide explodes. When, however, a mixture of nitric oxide and hydrogen is passed over heated platinum black, ammonia is formed ($2NO + 5H_2 = 2NH_3 + 2H_2O$). Mixed with the vapour of carbon disulphide, it burns with an intensely blue light of great chemical activity.

Phosphorus and potassium (but not sodium), when heated, burn in the gas. It is also decomposed in the presence of moisture by red-hot iron and tin, the residual gas (nitrogen) constituting in each case one-half the volume of the original gas. Moist iron and moist zinc slowly decompose it, nitrous oxide (N_2O) being formed.

Solutions of *ferrous* and *chromous* salts absorb it freely, forming a dark olive-brown compound, consisting of four parts of a ferrous (or chromous) salt with two parts of nitrous oxide ($4FeSO_4,2NO$) (Péligot). These solutions absorb oxygen freely, and, when heated, evolve their nitric oxide unchanged.

Other metallic salts (such as stannous and mercurous salts) also absorb the gas, but with mutual decomposition. They cannot therefore, as in the case of ferrous and chromous salts, yield the nitric oxide after absorption in an unchanged state.

When nitric oxide is passed into an alkaline solution of a sulphite, an alkaline salt of dinitroso-sulphonic acid ($H_2SO_3(NO)_2$) is formed. The free acid has not been prepared, the salts undergoing decomposition into sulphates and nitrous oxide ($K_2SO_3(NO)_2 = K_2SO_4 + N_2O$).

The gas is absorbed by nitric acid, a red, green, or blue solution (according to the dilution of the acid) resulting. Probably in these cases a higher nitrogen oxide (N_2O_4) is formed.

Nitric oxide has a basylous character, and, like the alkaline metals, is capable of replacing hydrogen in many compounds. Thus, like sodium, it will replace one of the hydrogens of alcohol:—

$C_2H_5(OH)$; — $C_2H_5(ONa)$; — $C_2H_5(O(NO))$.
Alcohol — Sodic ethylate — Nitrous ether.

The compounds $NOCl$ and $NOCl_2$ may be regarded as chlorides of nitric oxide. (See page 147.)

It is used as a test for the presence of free oxygen.

Nitrous Anhydride (N_2O_3).

Molecular weight (*probable*) 76. *Molecular volume, probable* ☐☐.
Specific gravity (*theoretic*) 2·63.

Synonyms.—*Nitrous acid* (Davy, Graham, Gmelin, Berzelius, Miller) ; *Pernitrous acid* (Gay Lussac) ; *Hyponitrous acid* (Turner, Brande, and Liebig); *Nitrous oxide* (Watts); *Nitric trioxide* (Roscoe); *Nitrogen trioxide* (Fownes, Roscoe).

Preparation.—(1.) By mixing four volumes of *dry* nitric oxide with one volume of dry oxygen, and cooling the mixture to 0° F (—18° C.), ($2NO + O = N_2O_3$).

(2.) By the action of arsenious anhydride upon nitric acid :—

$As_2O_3 + 2HNO_3 = As_2O_5 \quad H_2O + N_2O_3$
Arsenious anhydride + Nitric acid = Arsenic anhydride + Water + Nitrous anhydride

(3.) By the action of strong nitric acid on silver :—

$6HNO_3 + 2Ag_2 = 4AgNO_3 + 3H_2O + N_2O_3$.
Nitric acid + Silver = Argentic nitrate + Water + Nitrous anhydride.

(4.) By heating one part of starch, sugar, or other easily oxidizable body, with eight parts of nitric acid (1·2 specific gravity).

Properties.—(*a.*) *Sensible and Physical.*—A deep red gas, condensing at 0° F. (—17·8° C.) to a blue liquid, which evolves red fumes even at 28·4° F. (—2° C.). The liquid at 14·0° F. (—10° C.) becomes of a deep indigo color.

(β.) *Chemical.* — Nitrous anhydride combines with sulphurous anhydride to form the white flakes of the oil of vitriol leaden chamber ($2SO_3+N_2O_3$). The gas is soluble in nitric acid, forming a coloured solution. By the action of *a little ice cold water* on the gas, nitrous acid is formed, the liquid becoming blue ($N_2O_3+H_2O=2HNO_2$). On the *addition of an excess of water even at ordinary temperatures*, it is decomposed into nitric acid and nitric oxide ($3N_2O_3+H_2O=2HNO_3+4NO_2$).

Nitrous Acid (HNO_2).

Molecular weight, 47.

Preparation.—(1.) By mixing a little ice cold water with nitrous anhydride—

$$\begin{array}{cccccc} N_2O_3 & + & H_2O & = & 2HNO_2. \\ \text{Nitrous anhydride} & + & \text{Water} & = & \text{Nitrous acid.} \end{array}$$

(2.) By the oxidation of ammonia; as, *e.g.*, by placing a red-hot platinum wire in a mixture of air and ammonia gas, or by shaking up a few drops of ammonia solution with metallic copper in a bottle containing air. (Schönbein.)

Properties.—Nitrous acid is an ill-defined and unstable compound. It forms salts called nitrites which are stable. Of these salts, as of the acid itself, our knowledge is imperfect. Potassic nitrite (KNO_2) is obtained by heating potassic nitrate (KNO_3) so as to drive off some of its oxygen. Nitrous acid imparts the red colour to nitric acid that it acquires on exposure to light. It is decomposed by water into nitric acid and nitric oxide ($3HNO_2=HNO_3+2NO+H_2O$).

The acid, as well as acidulated solutions of the nitrites, act both as reducing and as oxidizing agents, thus—

(*a.*) As an *oxidizing* agent ($4HNO_2=4NO+2H_2O+O_2$) the acid decolorizes indigo, converts ferrous into ferric salts, oxidizes iodides, and liberates iodine from potassic iodide.

(β.) As a *reducing* agent ($2HNO_2+O_2=2HNO_3$) its action may be seen in its effect on permanganates and chromates, and also in setting free metallic gold and mercury from their combinations.

Nitric Peroxide (N_2O_4 and at high temperatures, NO_2).

Molecular weight, 46 *and* 92; *Molecular volume*, $\boxed{}\boxed{}$. *Specific gravity at* 309·2° F. (154° C.)=1·58. 1 *litre weighs* (0·0896 × 23)= 2·06 *grms.*, *or* (0·0896 × 46)=4·12 *grms.*

Synonyms.—*Nitrous acid* (Turner, Brande, etc.); *Hyponitric acid* (Gmelin); *Nitrous gas* (Berzelius); *Peroxide of nitrogen* (Graham, Odling, etc.); *Pernitric oxide; Nitrogen tetroxide* (Roscoe); *Nitryl* (because of its basylous action; thus allying it to hydroxyl).

History.—First obtained by mixing together nitric oxide and oxygen. (Davy.)

Preparation.— (1.) By submitting a mixture of two parts of nitric oxide and one part of oxygen to a freezing mixture. (Péligot.)

(2.) By heating very dry plumbic nitrate. (The N_2O_4 thus produced is mixed with one-fourth its volume of oxygen.)

$$2(Pb2NO_3) = 2PbO + 2N_2O_4 + O_2.$$

Plumbic Nitrate = Plumbic oxide + Nitric peroxide + Oxygen.

(3.) By the action of tin on nitric acid :—

$$Sn_5 + 20HNO_3 = Sn_5O_{10},5H_2O + 5H_2O + 10N_2O_4.$$

Tin + Nitric acid = Metastannic acid + Water + Nitric peroxide.

(4.) By heating to 104·0° F. (40° C.) a mixture of nitrosyl chloride and argentic nitrite :—(Exner.)

$$NO_2Cl + AgNO_2 = AgCl + N_2O_4$$

Nitrosyl chloride + Argentic nitrite = Argentic chloride + Nitric peroxide.

(5.) By gently heating a mixture of nitric acid (1·39) and arsenious acid and condensing the gaseous N_2O_3 and N_2O_4 evolved. A current of oxygen must be passed through the liquid to convert the N_2O_3 into N_2O_4. (Hassenbach.)

$$As_2O_3 + 4HNO_3 = As_2O_5 + 2H_2O + 2N_2O_4$$

Arsenious anhydride + Nitric acid = Arsenic anhydride + Water + Nitric peroxide.

Properties.—(*a.*) *Sensible and Physiological.*—A brownish red gas, very irritating when inhaled. It stains the skin a yellow colour.

(*β.*) *Physical.*—Its relative weight (*i.e.*, its weight compared with hydrogen at the same temperature) diminishes with a rise of temperature. At low temperatures its density is 46 (*i.e.*, it is 46 times as heavy as hydrogen), the molecule being represented by N_2O_4, whilst at 309·2° F. (154° C.) this molecule of N_2O_4 is split up (dissociated) into two molecules of NO_2, with a density of 23.

Actual experiments give the following results (Deville and Troos) :—

At	80·0° F.	(26·7° C.)	Specific Gravity	2·65.
,,	140·3° F.	(60·2° C.)	,,	2·08.
,,	1770·° F.	(80·6° C.)	,,	1·80.
,,	212·1° F.	(100·1° C.)	,,	1·68.
,,	309·2° F.	(154·0° C.)	,,	1·58.
,,	361·	(183·2° C.)	,,	1·57.

Thus it would seem that the molecule of nitric peroxide is differently constituted at different temperatures, the N_2O_4 being completely dissociated above 154° C.

The absorption spectrum of nitric peroxide is characteristic.

Action of heat.—When the gas is perfectly dry, a cold of 0° F. (—17·8° C.) condenses it into colorless, transparent, prismatic crystals. These crystals melt at 14° F. (—10° C.), forming a colorless and corrosive liquid, which gradually changes to a green liquid as the temperature rises to 71·6° F. (22·6° C.), when it boils.

The liquid has a specific gravity of 1·451. It cannot be solidified a second time at a temperature above —22° F. (—30° C.).

By the action of heat, the vapor becomes gradually darker until at 104° F. (40° C.) it is almost black. It is decomposed by electric sparks, and by a temperature above red heat. The action of water upon it will be studied under its chemical properties.

(γ.) *Chemical.*—Its composition may be determined by passing the vapor of a known weight of the gas over a weighed quantity of red hot copper. The increase in the weight of the copper gives the oxygen, the residual gas being nitrogen mixed with a little nitric oxide which must be estimated.

Nitric peroxide reddens litmus. It was long considered an anhydride, but it always forms with bases, a mixture of a nitrite and nitrate.

It does not support the combustion of bodies unless they be burning energetically when introduced. Chlorine combines with it indirectly but not directly, to form an oily liquid called chloride of nitryl (NO_2Cl).

When a mixture of nitric peroxide and hydrogen is passed over spongy platinum, the nitric peroxide is decomposed with elevation of temperature, water and ammonia being formed ($N_2O_4+7H_2=2NH_3+4H_2O$). When a mixture of sulphuretted hydrogen with the gas is similarly treated, water and ammonia are formed, and sulphur precipitated ($N_2O_4+7H_2S=2NH_3+4H_2O+7S$).

Its *action on water* is remarkable. If a trace of moisture be present when the gas is subjected to the freezing mixture, it forms a green liquid, having the probable formula of (N_2O_3,N_2O_5,H_2O). This green liquid becomes yellow at 14° F. (10° C.), and red at ordinary temperatures. It freezes at —40° F. (—40° C.), and boils at 82° F. (28° C.) Like liquid nitric peroxide, it freely evolves red fumes at ordinary temperatures. But if a very little ice cold water be added to the liquid nitric peroxide at 0° F. (—17·8° C.), two liquid layers are immediately formed, the *upper layer* being the least coloured, consisting of nitric acid, and *the lower layer*, the most coloured, consisting of nitrous acid and nitrous anhydride:—

$$\underset{\text{Nitric peroxide}}{3N_2O_4} + \underset{\text{Water}}{2H_2O} = \underset{\text{Nitric acid}}{3HNO_3} + \underset{\text{Nitrous acid}}{HNO_2} + \underset{\text{Nitrous anhydride.}}{N_2O_3}$$

If at this low temperature more water be added to the liquid, nothing but nitrous and nitric acids remain:—

$$\underset{\text{Nitric peroxide}}{N_2O_4} + \underset{\text{Water}}{H_2O} = \underset{\text{Nitric acid}}{HNO_3} + \underset{\text{Nitrous acid.}}{HNO_2}$$

If water be added to the liquid peroxide *at ordinary temperatures*, the solution passes through various shades of color, viz., orange, yellow, green, and blue, finally becoming colorless, an escape of nitric oxide taking place all the time :—

$3N_2O_4$	+	$2H_2O$	=	$4HNO_3$	+	N_2O_2.
Nitric peroxide	+	Water	=	Nitric acid	+	Nitric oxide.

Thus, it would seem that a variety of decompositions may be effected, according (α) to the proportion of water mixed with the nitric peroxide, and (β) the temperature of the water added, but that in every case nitric acid is formed. These reactions may be thus tabulated—

Cold of 0° F.(-17·4° C.)	$4N_2O_4 + H_2O$	=	$2HNO_3$	+	N_2O_5	+	$2N_2O_3$
			Nitric acid		Nitric anhydride		Nitrous anhydride
	$3N_2O_4 + 2H_2O$	=	$3HNO_3$	+	HNO_2	+	N_2O_3
			Nitric acid		Nitrous acid		Nitrous anhydride
	$3N_2O_4 + 3H_2O$	=	$3HNO_3$	+	$3HNO_2$		
			Nitric acid		Nitrous acid		
Ordinary temperature	$3N_2O_4 + 2H_2O$	=	$4HNO_3$	+	N_2O_2		
			Nitric acid		Nitric oxide		

Action of Acids.—Sulphuric acid absorbs the gas, forming a crystalline compound, nitro-sulphonic acid (SO_2NO_2HO), which by the action of water is resolved into sulphuric acid, nitric oxide, and nitric peroxide. Heated with liquid sulphurous acid in sealed tubes, nitric peroxide forms the crystalline compound ($S_2O_52NO_2$ = dinitryl of disulphuric acid, or the anhydride of nitro-sulphonic acid). Nitric acid dissolves it, and forms the deep red, green, and blue liquids, known in commerce as "nitric acid fortissimus." The color of these liquids is destroyed by dilution. Hydrochloric acid forms with it several chlorinated compounds.

Action on the Metals and their Compounds.—Most metals are oxidized by it. Potassium takes fire in it spontaneously. Iron decomposes it at a red heat, evolving nitrogen. Potassium, lead, mercury, etc., form a nitrate with the liquid peroxide, nitric oxide being expelled ($2N_2O_4 + K_2 = 2KNO_3 + N_2O_2$). With metallic oxides and hydrates a nitrate and a nitrite of the metal are formed :—

N_2O_4	+	$2HKO$	=	KNO_3	+	KNO_2	+	H_2O.
Nitric peroxide	+	Potassic hydrate	=	Potassic nitrate	+	Potassic nitrite	+	Water.

With potassic sulphocyanide (like ferric salts) nitric peroxide gives a red color, the solution, however (unlike the ferric reaction) rapidly losing its color. This reaction distinguishes peroxide of nitrogen from nitrous acid.

Action of Organic Bodies.—In some cases nitric peroxide combines directly with the organic body ; thus C_5H_{10} (*Amylene*) + N_2O_4 = C_5H_{10},N_2O_4. In other cases it replaces hydrogen, forming nitro compounds which are often explosive. They are produced by the direct action of *fuming* nitric acid (mixed with sulphuric acid in order to increase its strength) on the organic body. The following are illustrations :—

		Nitro Compounds.	
Benzole C_6H_6	forms	$C_6H_5(NO_2)$	Nitro-benzole.
,,	,,	$C_6H_42(NO_2)$	Dinitro-benzole.
Napthalene $C_{10}H_8$	,,	$C_{10}H_7(NO_2)$	Nitro-naphthalene.
Glycerine $C_3H_8O_3$	,,	$C_3H_53(NO_2)O_3$	Nitro-glycerine.
Mannite $C_6H_{14}O_6$	,,	$C_6H_86(NO_2)O_6$	Nitro-mannite.
Cellulose $C_6H_{10}O_5$	,,	$C_6H_82(NO_2)O_5$	Nitro-cellulose.
Starch $C_{12}H_{20}O_{10}$	,,	$C_{12}H_{19}(NO_2)O_{10}$	Xyloidin.

General Remarks on the Oxides of Nitrogen.

Before we proceed to examine the next oxide of nitrogen, it is well that we should generalise on certain facts relative to the oxides of nitrogen thus far investigated. Note, then—

(1.) That the proportions of oxygen in the series advance in a regularly ascending order—N_2O, N_2O_2, N_2O_3, N_2O_4.

(2.) That the names of the oxides are very confusing.

(3.) That they have all been discovered since the time of Priestley (1776).

(4.) That none of them occur free in nature, and that only one (viz., N_2O_3 as nitrites) has even been found in a combined state.

(5.) That they may all be prepared by the deoxidation and dehydration of nitric acid, and that two of them (viz., N_2O_3 and N_2O_4) may be prepared by the oxidation of NO.

This may be shown thus :—

$$2\,HNO_3 - H_2O - O = N_2O_4 \text{ Nitric peroxide.}$$
$$2\,HNO_3 - H_2O - O_2 = N_2O_3 \text{ Nitrous anhydride.}$$
$$2\,HNO_3 - H_2O - O_3 = N_2O_2 \text{ Nitric oxide.}$$
$$2\,HNO_3 - H_2O - O_4 = N_2O \text{ Nitrous oxide.}$$

We may thus summarise the preparation of the nitrogen oxides :—

(i.) N_2O_4 is prepared by the action of *tin* on nitric acid :—

$$20HNO_3 + Sn_5 = Sn_5O_{10},\ 5H_2O + 5H_2O + 10N_2O_4.$$

(ii.) N_2O_3 is prepared by the action of *silver* on nitric acid :—

$$6HNO_3 + 2Ag_2 = 4AgNO_3 + 3H_2O + N_2O_3.$$

(iii.) NO is prepared by the action of *copper* on nitric acid (Specific Gravity 1·25) :—

$$8HNO_3 + 3Cu = 3CuN_2O_6 + 4H_2O + 2NO.$$

(iv.) N_2O is prepared by the action of *zinc* on nitric acid :—

$$10HNO_3 + 4Zn = 4ZnN_2O_6 + 5H_2O + N_2O.$$

(6.) That at common temperatures they are all gases, the first two of the series (viz., N_2O and NO) being colorless, and the last two red. One (viz., N_2O) is respirable, and the others are irrespirable.

(7.) That in N_2O_4 the molecule is differently constituted at different temperatures.

(8.) That at high temperatures they may all be decomposed, when combustible bodies burn in them.

(9.) *Action of Metals.*—They are all decomposed by the alkaline metals, and also by metallic iron and zinc when heated in contact with them.

(10.) *Action of Water.*—The first two (N_2O and NO) of the series are soluble in water, whilst the remaining two (viz., N_2O_3 and N_2O_4) are decomposed by water into nitric acid and other nitrogen oxides.

(11.) *Action of Acids.*—*Sulphuric acid* is without action upon them. *Sulphuric anhydride* unites with N_2O_3 and N_2O_4 to form the white flakes of the oil of vitriol leaden chamber. *Nitric acid* forms dark colored liquids with NO, N_2O_3, and N_2O_4.

(12.) Two of them (viz., NO and N_2O_4) are *basylous* in character, either (α) combining with chlorine to form chlorides (as *e.g.* NO), or (β) displacing hydrogen in organic compounds (as *e.g.* NO_2).

(13.) Nitrous oxide is employed as an anæsthetic, but the other members of the series have little use other than the part they play in the manufacture of oil of vitriol.

(14.) That they all (like ozone) set iodine free from potassic iodide.

Nitric Anhydride, N_2O_5.

Molecular weight (*probable*) 108. *Molecular volume* (*probable*) ☐☐.
Melts at 85° F. (29·5° C.). *Boils at* 113° F. (45° C.).

Synonyms.—*Nitrogen pentoxide—Dinitric pentoxide.*

History.—First prepared by Deville in 1848.

Preparation.—(1.) By passing very dry chlorine over hot argentic nitrate. (Deville.) (*Ann. Chim. Phys.*, 1850 [3], xxviii., 241.)

$4AgNO_3$	+	$2Cl_2$	=	4AgCl	+	$2N_2O_5$	+	O_2
Argentic nitrate	+	Chlorine	=	Argentic chloride	+	Nitric anhydride	+	Oxygen.

The silver salt must be first heated to about 200° F. (93·5° C.) and afterwards kept at 150° F. (65·6° C.) The products are to be condensed in a cold receiver.

(2.) By passing the vapor of chloride of nitrosyl over argentic nitrate heated to 140° F. (60° C.). (Odet and Vignon.)

NO_2Cl	+	$AgNO_3$	=	AgCl	+	N_2O_5.
Chloride of nitrosyl	+	Argentic nitrate	=	Argentic chloride	+	Nitric anhydride.

(3.) By dehydrating nitric acid with phosphoric anhydride, the mixture being afterwards cooled to 0° C. and distilled. (Weber and Berthelot.)

$$\underset{\text{Nitric acid}}{6HNO_3} + \underset{\text{Phosphoric anhydride}}{P_2O_5} = \underset{\text{Phosphoric acid}}{2H_3PO_4} + \underset{\text{Nitric anhydride.}}{3N_2O_5.}$$

Properties.—A colorless volatile solid (density 1·64), crystallising in rhombic or six-sided prisms. It turns yellow when heated to 248° F. (120° C.). It melts at 85° F. (29·5° C.), and boils at 113° F. (45° C.) It is a very unstable body, and is decomposed by a heat of 122° F. (50° C.), or by exposure to direct sunlight. Sometimes it explodes spontaneously. It volatilizes unchanged in dry air, whilst in moist air it deliquesces with the formation of nitric acid. It unites energetically with water to form nitric acid, the combination being attended by great elevation of temperature. A crystalline hydrate (N_2O_5, $2HNO_3$, specific gravity 1·642) is formed by dissolving N_2O_5 in strong nitric acid. With sulphur it forms white vapours of nitro-sulphuric anhydride ($S_2O_5(NO_2)_2$).

Nitric Acid ($HNO_3 = 63$).

Molecular weight, 63. *Molecular volume,* $\boxed{\ \ }\boxed{\ \ }$. 1 *litre of nitric acid vapor weighs* 31·5 *criths* (0·0896 × 31·5) = 2·821 *grms., and* 100 *cubic inches* 68·00 *grains.*

Synonyms.—*Aqua Fortis* (Alchymists); *Solutive Water* (Geber); *Spirit of Nitre* [*Spiritus nitri fumans Glauberi*] (Glauber); *Hydric Nitrate; Hydrogen Nitrate* (Watts in Fownes).

History.—Nitric acid was known to the alchymists at a very early period. Mayow (1669) regarded it as a compound of a fiery element derived from the air with an earthy component. Lavoisier (1776) proved oxygen to be one of its constituents. Priestley (1777) noticed its formation when electrical sparks were passed through air. Cavendish (1785) remarked on the acidity of the product formed when hydrogen was burnt in air, which acidity he considered due to the presence of nitric acid. He also remarked on the formation of nitre when electrical discharges were passed through a mixture of nitrogen and oxygen standing over soap-lees (caustic potash). (*Phil. Trans.*, 1785, p. 379.) Thus its composition was determined. Davy, Gay Lussac, and Thompson determined the proportions in which nitrogen and oxygen were present in the acid.

Natural History.—(*a.*) *In the mineral kingdom,* it is found as nitre; soda or cubic nitre ($NaNO_3$) being obtained from Chili, and potash or prismatic nitre (KNO_3) from India. These are formed by the rapid oxidation of organic nitrogenized bodies, such as the urea of urine, etc., under the influence of a tropical heat, and in the presence of soils rich in alkalies. It is also found as nitrates in many well waters, produced by the oxidation of nitrogenized matters as they percolate in solution through the soil. Nitrate of ammonia, moreover, is found in rain water, atmospheric electricity effecting the combination of the nitrogen and oxygen, the nitric acid formed in the presence of moisture combining with ammonia. Nitrate of lime ($Ca2NO_3$) is often found as an efflorescence on the walls of cellars, stables, etc. (*b.*) *In the vegetable kingdom,* nitric acid is not found in the recent juices of plants, but it occurs in dried leaves (*e.g.,* in those of tobacco), arising from the decomposition of the alkaloids and the oxidation of their nitrogen. (*c.*) *In the animal kingdom,* it is not a common constituent except in the urine after the administration of ammonia.

Preparation.—(1.) By the direct union of oxygen and nitrogen.

(*a.*) By the passage of the sparks from an induction coil through air (particularly if compressed), or through a mixture of two volumes of nitrogen and five volumes of oxygen. Red fumes of N_2O_4 are rapidly formed (recognisable by starch and iodide paper), and if these be shaken up with a little water, nitric acid will be found in the solution. [Thus nitric acid is formed in the air by electrical discharges.]

(*b.*) By burning ammonia, or a mixture of one part of nitrogen and ten parts of hydrogen, in air or oxygen. The water formed will be found to contain traces of nitric acid.

(2.) By treating nitrous anhydride (N_2O_3) and nitric peroxide N_2O_4) with water (*see* pages 134, 136).

(3.) By the slow oxidation of organic matter containing nitrogen [or of ammonia] in the presence of an alkali, of moisture at a temperature of about 77° F. (25° C.), and possibly of a special kind of bacterium (?).

(4.) *Ordinary manufacturing process.*—By distilling a mixture of potassic or sodic nitrate with strong sulphuric acid in cast-iron cylinders.

[A wetted coke scrubber is usually attached to the apparatus in order to absorb any nitric peroxide that may escape the condensers during the operation.]

The decomposition is two-fold :—

(*a.*) The sulphuric acid displaces one-half the nitric acid—

H_2SO_4	+	$2NaNO_3$	=	$NaNO_3$	+	$NaHSO_4$	+	HNO_3.
Sulphuric acid	+	Sodium nitrate	=	Sodium nitrate	+	Hydric sodium sulphate (bisulphate of soda)	+	Nitric acid.

(*b.*) By an increased temperature the hydric sodium sulphate formed decomposes the remaining sodium nitrate—

$NaNO_3$	+	$NaHSO_4$	=	Na_2SO_4	+	HNO_3.
Sodium nitrate	+	Hydric sodium sulphate	=	Sodium sulphate	+	Nitric acid.

The sodic nitrate (cubic or Chili nitre) is ordinarily used in the nitric acid manufacture because (*a,*) it is *cheaper* than potassic nitrate, and (*b*,) yields *a larger percentage* of acid owing to the lower atomic weight of sodium. The sodic sulphate left in the retort is used in glass manufacture.

Impurities.—Lower oxides of nitrogen, owing to the decomposition effected by the high temperature employed in the second part of the operation; chlorine, and iodine as iodic acid (derived from the alkaline chlorides and iodides in the nitre); sulphuric acid; iron oxide; alumina; potash and soda salts.

Preparation of Pure Acid.—To purify the acid commercially, and to increase its strength (*i.e.*, to obtain an acid containing 99·5 to 99·8 per cent. of HNO_3), it is re-distilled in glass retorts with its own bulk of strong sulphuric acid, the first distillate being rejected as liable to contain chlorine. The residue in the retort will contain sulphuric acid, sodic sulphate, and iodic acid. To free it from the lower nitrogen oxides, the distillate is warmed and air passed through it until cold.

To obtain a very pure acid proceed as follows:—Dilute the acid with its own bulk of water. Add one grain of potassic bichromate for every 100 grains of the strong acid, in order to oxidize any of the lower oxides of nitrogen. Add nitrate of silver to precipitate any chlorine. Syphon off the clear liquid and distil, rejecting the first half of the distillate.

The pure acid (1) leaves no fixed residue, and (2) gives no precipitate with either baric or argentic nitrate.

Properties.—(α.) *Sensible.*—When pure, nitric acid is a colorless liquid, fuming in the air. More often, however, the acid of commerce is yellow, from the presence (by decomposition) of nitrous acid or nitric peroxide. Its taste is powerfully acid, and it has a slight odour.

(β.) *Physiological.* It is an intensely irritant poison, and a powerful escharotic. When very dilute it colours the skin and other organic bodies yellow (Xantho-proteic reaction). Sodic carbonate or magnesia suspended in water are proper antidotes.

(γ.) *Physical.* Its specific gravity varies according to its strength (*see* Table I. in Appendix). It forms grey fumes when exposed to the air, the acid absorbing water, and condensing into minute drops. When an acid of any gravity is boiled for some time, an acid of a definite strength results, the stronger acid losing its acid, and the weaker acid its water. This standard acid is represented by the formula $2HNO_3+3H_2O$, and is the acid of the Pharmacopœia, having a specific gravity of 1·42. The strongest acid has a gravity of 1·53, and is prepared with well-dried Chili saltpetre and sulphuric acid of a specific gravity of 1·85. It mixes with water in all proportions, heat being evolved. "Fuming nitric acid" is the strongest nitric acid (Sp. Gr. 1·53), in which the nitric peroxide has not been driven off.

Action of Heat.—The strong acid (1·5) boils at 186·8° F. (86·0° C.), and an acid of specific gravity 1·42 (68%) at 248° F. (120° C.). At

186·8° F. (86° C.) the strong acid begins to decompose ($2HNO_3 = 2NO_2 + H_2O + O$). When heated in closed glass tubes to a temperature of 500° F. (260° C.) it is entirely decomposed ($2HNO_3 = 2N + H_2O + 5O$). The strong acid (specific gravity 1·5) freezes at —40° F. (—40° C.), becoming an acid of specific gravity 1·4 at —41° F. (—40·55° C.). The frozen acid has the appearance of a white buttery mass.

If, under ordinary pressure, an acid containing less than 70 per cent. be heated below 248° F. (120° C.), the distillate is stronger than the acid. At 248° F. (120° C.) the composition of the distillate becomes constant (viz., Sp. Gr. 1·42, containing 68 per cent. of pure acid). But with a change of pressure there comes a change in the composition of the distillate, there being a constant for each increase or decrease of pressure.

Action of Light.—The acid is decomposed by light into nitric peroxide, water and oxygen, the solution becoming more or less yellow ($2HNO_3 = 2NO_2 + H_2O + O$).

(δ.) *Chemical.* Nitric acid reddens litmus. It is a monobasic acid, forming normal salts only (nitrates), having the formula $M'NO_3$. It acts as a powerful oxidizing agent, owing to the large amount of oxygen it contains ($\frac{3}{4}$ of its weight), and the ease with which it can part with it. Thus by its action iodine, phosphorus, sulphur, selenium, carbon, boron, and silicon are converted into their highest oxy-acids, whilst the lower oxides, such as sulphurous, arsenious, and phosphorous acids, are at once converted into higher oxygen acids.

Action of Acids.—*Sulphuric acid* has no action upon nitric acid except dehydration. *Hydrochloric acid* decomposes it, forming aqua regia, or nitro-hydrochloric acid (3 of hydrochloric and 1 of nitric acid), a solution containing chlorine and the body called chloride of nitrosyl ($HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2$). When aqua regia is heated, it evolves nitric oxide and chlorine, which latter, in the nascent state, dissolves gold and platinum ($NOCl + Cl_2 + Au = NO + AuCl_3$).

Action on Metals and Metallic Oxides.—It may here be noted that when sulphuric acid acts on metallic zinc, or when hydrochloric acid acts on metallic iron or tin, free hydrogen is evolved:

$$H_2SO_4 + Zn = ZnSO_4 + H_2.$$
$$2HCl + Fe = FeCl_2 + H_2.$$

If sulphuric acid, however, acts on oxide of zinc, or hydrochloric acid acts on oxide of copper, the hydrogen is not liberated as free hydrogen, but in combination with oxygen, as water :—

$$H_2SO_4 + ZnO = ZnSO_4 + H_2O.$$
$$2HCl + CuO = CuCl_2 + H_2O.$$

When, however, nitric acid acts on metallic zinc or copper, no free hydrogen is evolved, because the oxygen which is liberated at the same time, effects, in the nascent state, the immediate oxidation of the hydrogen. The results, however, produced by the action of nitric acid on the metals vary. It will be noticed that the action of a dilute acid is more intense than that of a strong acid; whilst if the nitric acid contains nitrous acid, the oxidizing power of the acid is increased (because of the greater instability of the nitrous acid). On *the noble metals* (such as gold, platinum, iridium, rhodium, titanium, tantalum, etc.), it is without action. On *silver and palladium,* if the acid be dilute, and the liquid kept cool, no gas is evolved, nitrous acid, which remains in solution, being produced ($Ag_2 + 3HNO_3 = 2AgNO_3 + H_2O + HNO_2$). On *copper and mercury,* an acid of specific gravity 1·25 evolves nitric oxide (NO), ($3Cu + 8HNO_3 = 3CuN_2O_6 + 4H_2O + 2NO$), but an acid of specific gravity 1·42 evolves nitric peroxide (N_2O_4), ($Cu + 4HNO_3 = CuN_2O_6 + 2H_2O + N_2O_4$) ; whilst if the mixture of the nitric acid and the metal be heated, pure nitrogen will be disengaged ($5Cu + 12HNO_3 = 5CuN_2O_6 + N_2 + 6H_2O$). On *zinc* (upon which the action of nitric acid is energetic), a dilute acid yields nitrous oxide (N_2O), ($4Zn + 10HNO_3 = 4ZnN_2O_2 + 5H_2O + N_2O$), whilst a stronger acid sets free ammonia, which at once combines with any excess of acid present ($4Zn + 9HNO_3 = 4ZnN_2O_6 + 3H_2O + H_3N$). *Tin and antimony* are oxidized, but not dissolved, by nitric acid. In the case of tin, an insoluble stannic oxide (SnO_2) is formed, called *putty powder,* and nitric peroxide evolved ($Sn + 4HNO_3 = SnO_2 + 2H_2O + 2N_2O_4$).

On *bismuth, tin* and *iron* the strong acid (Sp. Gr. 1·5) has no action, but if a little water be added, energetic action at once commences. If iron, after having been immersed in the strong acid be taken out, and, without being wiped, is then placed in a weak acid, the iron will be found to have assumed *a passive state,* that is, the weak acid will have no further action upon it.

Heated with an *oxide* or a *metallic base,* nitric acid evolves no gas, but forms salts called nitrates ($CuO + 2HNO_3 = H_2O + CuN_2O_6$), all of which are soluble. (*See* NITRATES.)

Action on Organic Bodies.—Nitric acid destroys all organic bodies. It oxidizes turpentine with explosive violence. Dropped on hot and finely powdered charcoal, the charcoal burns vividly. It stains all albuminous substances yellow. When added to morphia, brucia, or narcotine they are turned red. It oxidizes and bleaches indigo (C_2H_5NO), changing it into isatin ($C_2H_5NO_2$). Substitution compounds, more or less combustible, are formed by the action of the strong acid on certain organic bodies.

Tests. (*a.*) *In a free state.*

(1.) The production of red fumes (N_2O_4) when heated with the metals (*e.g.* copper).

(2.) Its power of reddening morphia, brucia, etc.

(3.) The formation of a red or brown colour (dependent on the quantity of nitric acid present) when brought into contact with a mixture of aniline and sulphuric acid. (Braun.)

(β.) *In a combined state* (as nitrates). [All nitrates are decomposed by strong sulphuric acid, yielding free nitric acid.]

(1.) Add to the nitrate some sulphuric acid to liberate nitric acid, and float on the mixture a solution of ferrous sulphate. A part of the nitric acid will be reduced, the ferrous becoming ferric sulphate, whilst the remainder of the ferrous sulphate solution will absorb the lower oxides of nitrogen set free, and the solution become brown where the two liquids touch, a compound of ferrous sulphate and nitric oxide being formed. (Liebig.)

(2.) Add to the solution of a nitrate, sulphuric acid and a little indigo solution; the latter will be bleached by the nitric acid liberated by the action of the sulphuric acid on the salt.

(3.) By adding sulphuric acid to a nitrate and shaking the mixture with mercury, NO is set free, the quantity evolved indicating the amount of nitric acid present (Crum's test as modified by Frankland).

(4.) A nitrate placed on red-hot charcoal deflagrates. (Chlorates act similarly.)

For quantitative determination, etc., see NITRATES.

Uses.—(*a.*) *In nature* nitric acid is one of the sources of the nitrogen of plants. It is of no special use to animals. (*b.*) *In chemistry and in the arts* its chief use is as a solvent and as an oxidizer, *e.g.*, in the manufacture of gun cotton and nitro-glycerine, the coal-tar colours, sulphuric acid, and in the preparation of the nitrates, such as those of silver (used in photography), of barium and strontium (used in pyrotechny), of iron, lead, and aluminium (used in dyeing and calico printing), etc. (*c.*) *In medicine* we have in the B.P. the *acidum nitricum* (specific gravity 1·42, and containing 70 per cent. of HNO_3, being in reality $2HNO_3,3H_2O$) and *acidum nitricum dilutum* (Sp. Gr. 1·101), containing 17·44 per cent. of HNO_3. The strong acid (Sp. Gr. 1·5) is used as an escharotic.

COMPOUNDS OF NITROGEN AND THE HALOIDS.

The combination of nitrogen with the haloids cannot be effected directly, whilst there is some doubt as to whether any such compounds exist without the presence of hydrogen.

1. COMPOUNDS OF NITROGEN AND FLUORINE.

No compound of nitrogen with fluorine is known without hydrogen (NH_4F).

2. COMPOUNDS OF NITROGEN AND CHLORINE.

Chloride of Nitrogen (*Nitrous Chloride*), $NCl_3 = 120·5$.

Of the composition of this body there is considerable doubt, its analysis being rendered difficult on account of its explosive nature.

Some regard it as NCl_3, and others as a compound of $NHCl_2$ + NCl_3. In the former case it is regarded as an ammonia molecule, where three atoms of hydrogen are replaced by three of chlorine; in the latter as a double ammonia molecule, where five hydrogens are replaced by five chlorines, one hydrogen not being disturbed. Possibly there may be a series of these compounds, such as NH_2Cl, $NHCl_2$, NCl_3.

History.—Discovered by Dulong in 1812; investigated by Davy.

Preparation.—(1.) By the action of chlorine on a strong solution of ammonic chloride at 86° F. (30° C.):—

$$NH_4Cl + 3Cl_2 = 4HCl + NCl_3.$$

Ammonium Chloride + Chlorine = Hydrochloric acid + Chloride of nitrogen.

[NOTE.—The action of chlorine on an *excess* of ammonia is to set free nitrogen ($8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$). When ammonia gas burns in chlorine, hydrochloric acid and nitrogen are formed.]

(2.) By the electrolysis of ammonium chloride. The chlorine developed at the + pole, becomes chloride of nitrogen.

Properties.—(*a.*) *Sensible.*—An oily liquid (like olive oil) having a peculiar odor; irritating to the eyes and nose.

(β.) *Physical.*—Specific gravity 1·653. It is volatile at ordinary temperatures, and boils at 160° F. (71·1° C.). It does not freeze at —16·6° F. (—27° C.). It explodes violently at from 200° to 212° F. (93° to 100° C.)

(γ.) *Chemical.*—The elements in chloride of nitrogen are very feebly combined. A slight warmth, the mere contact of phosphorus, sulphur, arsenic, the alkalies, or of inflammable bodies generally (such as fat or turpentine) cause its immediate explosion. The metals, the mineral acids, alcohol, and water have no action upon it.

3. COMPOUNDS OF NITROGEN AND BROMINE.

It is doubtful whether any compound of these bodies exists. Millon in 1828 remarked that potassic bromide decomposed nitrous chloride (NCl_3), forming a red liquid having similar properties to the chloride of nitrogen. He considered that the Cl_3 had been replaced by Br_3.

4. COMPOUNDS OF NITROGEN AND IODINE.

Iodide of Nitrogen (*Nitrous Iodide*, NI_3).

Of the composition of this body there is much doubt. Possibly there is a series of compounds, of which Gladstone and Frankland mention NHI_2 (nitrous hydrobiniodide), and Bunsen (NI_3, NH_3).

Preparation.—By the action of iodine on ammonia:—

$$4NH_3 + 3I_2 = NI_3 + 3NH_4I$$

Ammonia + Iodine = Nitrous Iodide + Ammonic Iodide

NOTE.—Nitrogen is liberated by the action of chlorine and bromine (but not by the action of iodine) on ammonia.

Properties.—A black powder having an iodine smell and a very high specific gravity. When dry it is easily decomposed by heat or by the touch of a feather, fumes of iodine vapor being liberated ($NHI_2=N+HI+I$). *Water* dissolves and decomposes it, forming an ammonic iodate, iodine with a little free nitrogen being evolved. *Sulphuretted hydrogen* decomposes it, ammonic iodide, hydriodic acid, and sulphur being formed ($NHI_2+2H_2S=NH_4I+HI+S_2$). It is also decomposed by solutions of the alkalies and of the alkaline earths, iodides and iodates being formed.

COMPOUNDS OF NITROGEN WITH OXYGEN AND THE HALOIDS.

Nitrous Oxychloride, NOCl.

Molecular weight, 65·5. *Molecular volume*, $\square\square$. *Relative weight*, 32·67. *Specific gravity*, *theoretic* 2·2663, *observed* 2·29. 1 *litre weighs* (32·75 *criths*) 2·9344 *grms. and* 100 *cubic inches* 70·18 *grains.*

Synonyms.—*Chloro-nitrous gas; nitrosyl chloride; azotyl chloride.*

Preparation. (1.) By the direct union of two volumes of nitric oxide and one volume of chlorine.

(2.) By heating a mixture of nitric (Sp. Gr. 1·42) and hydrochloric acids (Sp. Gr. 1·16) (aqua regia) :—

HNO_3	+	$3HCl$	=	$NOCl$	+	Cl_2	+	$2H_2O$.
Nitric acid	+	Hydrochloric acid	=	Nitrous oxychloride	+	Chlorine	+	Water.

[To obtain the pure chloride, pass the dried gases through strong ulphuric acid. The body $H(NO)SO_4$ (nitrosyl sulphate, or lead hamber crystals) is thus formed, Cl and HCl gases escaping. When the itrosyl sulphate is treated with an excess of dry sodium chloride, NOCl is evolved ($H(NO)SO_4+NaCl=NaHSO_4+NOCl$)].

(3.) By the action of phosphorus pentachloride on potassium itrite :—

PCl_5	+	KNO_2	=	$NOCl$	+	KCl	+	$POCl_3$
Phosphorus pentachloride	+	Potassium nitrite	=	Nitrous oxychloride	+	Potassic chloride.	+	Phosphorus oxytrichloride.

Properties.—An orange-colored gas, becoming a red liquid at 0° F. —18° C.), which boils at —17·2° F. (—8° C.). It is decomposed by ercury ($2NOCl+2Hg=Hg_2Cl_2+2NO$), and by contact with water $NOCl+H_2O=HNO_2+HCl$). With basic oxides, it forms a mixed itrite and chloride ($NOCl+2\,KHO=KNO_2+KCl+H_2O$).

A corresponding *nitrous oxybromide* or *nitrosyl bromide* (NOBr), a lackish brown liquid, and also a *nitrosyl tribromide* ($NOBr_3$) a brownish d liquid, are also known to exist.

Nitrylic Chloride ($NO_2Cl=81{\cdot}5$).

Relative weight 40·75. *Specific gravity of liquid*, 1·32 ; *of the vapor*, 2·63 (*theoretic*, 2·819).

Synonyms.—*Chloride of Nitryl—Nitric Dioxychloride—Chloropernitric gas—Nitroxyl Chloride—Chloride of Nitric Acid.*

Preparation.—(1.) By passing a mixture of chlorine and nitric peroxide through a hot tube ($NO_2+Cl=NO_2Cl$).

(2.) By the action of phosphorous oxychloride on plumbic or argentic nitrate (Odet and Vignon). [Some doubt has been thrown on this reaction by Mills.]

$3AgNO_3$	$+$	PCl_3O	$=$	Ag_3PO_4	$+$	$3NO_2Cl$.
Argentic nitrate	+	Phosphorous oxychloride	=	Argentic phosphate	+	Nitrylic chloride.

(3.) By the action of chlorhydrosulphuric acid on nitric acid (Williamson).

$HClSO_3$	$+$	HNO_3	$=$	H_2SO_4	$+$	NO_2Cl
Chlorhydrosulphuric acid	+	Nitric acid	=	Sulphuric acid	+	Nitrylic chloride.

Properties.—A heavy yellow liquid, boiling at 41° F. (5° C.) and not freezing at —23° F. (— 31° C.) It is decomposed by water into nitric and hydrochloric acids ($NO_2Cl+H_2O=HCl+HNO_3$).

Chloro-Nitric Gas, $NOCl_2$ or $N_2O_2Cl_4$.

Synonyms.—*Nitric dioxy-tetrachloride* (Frankland) ; *Nitric oxydichloride ; Azotyl bichloride.*

Preparation.—Formed, together with nitrous oxychloride, by heating aqua regia :—

$2HNO_3$	$+$	$6HCl$	$=$	$2NOCl_2$	$+$	$4H_2O$	$+$	Cl_2
Nitric acid	+	Hydrochloric acid	=	Chloro-nitric gas	+	Water	+	Chlorine.

Properties.—Below 19° F. (—7° C.) it is a red liquid, but above this temperature a yellow gas. It is decomposed by water or by an alkaline hydrate. With mercury it forms nitric oxide and mercurous chloride ($4Hg+N_2O_2Cl_4=2Hg_2Cl_2+N_2O_2$).

CHAPTER VII.

PHOSPHORUS.

PHOSPHORUS. Compounds of Phosphorus and Oxygen—Suboxide of Phosphorus—Hypophosphorous acid—Phosphorous anhydride—Phosphorous acid—Phosphoric anhydride—Metaphosphoric acid—Pyrophosphoric acid—Orthophosphoric acid—Compounds of Phosphorus and the Haloids—Phosphorous chloride—Phosphoric Chloride — Phosphoric Oxy-trichloride — Phosphoric Sulpho-trichloride—The Iodides of Phosphorus—Phospham—Action of Ammonia on Phosphorous Compounds.

PHOSPHORUS ($P = 31$).

Atomic weight 31. *Molecular weight* (31×4). *Atomic volume* $\square$ *or* $\frac{1}{2}$. *Molecular volume* $\boxed{\mid}$. *Atomicity pentad* (P_2O_5; PCl_5) *and triad* (PH_3 ; PCl_3). *Relative weight* ($H=1$), 62. *Specific gravity of vapor,* 4·2984. 1 *litre of phosphorus vapor weighs* (62 *criths, not* 31 *criths*) 5·555 *grms., and* 100 *cubic inches* 132·866 *grains.*

THE name *phosphorus* (φῶς and φέρω), equivalent to the Latin *ucifer,* is derived from its property of shining in the dark. The term ad been previously applied to various other bodies that were luminous vhen heated, viz., *Baldwin's phosphorus* (calcic nitrate), *Bolognian hosphorus* (baric sulphate), *Homberg's phosphorus* (fused calcic hloride), etc.

History.—Phosphorus was discovered accidentally by Brandt in rine during certain alchemical investigations (1669). He showed ome to a German chemist, Kunkel, who spoke of it to his friend Kraft. Kraft bought the secret of its preparation from Brandt for 00 dollars. Kunkel (1674) afterwards made it in sufficient quantity or sale, the material being known as "Kunkel's phosphorus." Boyle and his assistant, Godfrey Hankwitz (1680), also prepared it, he latter selling it under the name of "English Phosphorus." The rocess was improved by Margraaf (1740). Gahn, in 1768, discovered hosphorus in bones, and Scheele (1769) invented a ready process for reparing it therefrom, which was afterwards perfected by Fourcroy, Vauquelin, Nicholas, and Pelletier.

Ancient theories as to its nature.—Phosphorus was believed by the tahlians (their theory being in vogue at the time of its discovery) o be a compound of phlogiston and of the white fumes produced by its combustion. These white fumes were believed by Stahl to be muriatic acid, but this Margraaf, of Berlin, in 1740, proved to be an error, showing that the white flakes were phosphoric acid. The Stahlians then asserted that phosphorus was a compound of phosphoric acid and phlogiston. In 1772, Guyton Morveau proved that the phosphoric acid from burning phosphorus was heavier than the phosphorus from which it was obtained ; after which Lavoisier, in 1774-5, made his famous experiment of burning a known weight of phosphorus in a known quantity of oxygen, by which he proved phosphoric acid to be a compound of oxygen and phosphorus. In 1810-12, Davy, Gilbert, Gay Lussac, and Thénard, established its elementary nature, since which time its various allotropes have been discovered.

Natural History.—Phosphorus is never met with free in nature, but in a combined state only.

(α.) In the *mineral kingdom* it is found in all the primitive and volcanic rocks (chiefly as $Ca_3 2PO_4$), and in the soils produced by their disintegration. It occurs as osteolite, apatite and coprolite (phosphate of lime $Ca_3P_2O_8$), also as wavellite and massive phosphate of alumina, lead, uranium, etc. (β.) In the *vegetable kingdom* phosphorus is extracted from the soil by plants for animal use. It is found in all parts of the vegetable, but more particularly in the seed.

Quantity of Phosphoric Anhydride per cent. present in different substances.

	P_2O_5 per cent.
Ash of tobacco stalk	2·73
,, straw (barley, wheat, oats, &c.)	3·00
,, turnips	6·10
,, clover..	6·30
,, flax	10·77
,, potatoes	11·30
,, oats	14·90
,, wheat	16·40

(γ.) In the *animal kingdom* phosphorus is found in complex combinations in brain and nerve tissue, as though it were essential to the exercise of the higher functions. It is found in all the secretions, in urinary and in other calculi, in the tartar of the teeth thrown down from the saliva by the ammonia of the breath, etc.

Proportions of Phosphorus per cent. present in various animal tissues.

		Phosphorus per cent.
Mulder.	Dry fibrin	0·32—0·42.
	,, egg albumen ..	
	,, blood ,, ..	0·33.
Lassaigne.	Brain normal ..	1·93—1·97.
Courbe.	,, of idiots ..	1·00—1·50.
	,, of sane ..	2·00—2·50.
	,, of madmen ..	3·00—4·50.
	Bone..	16·96 = 53 per cent. of $Ca_3P_2O_8$.
	Solid matters of urine	2.32 per cent. of alkaline and earthy phosphates.

Preparation.—Phosphorus is the only element in the preparation of which animal substances are employed.

(1.) Preparation from urine (*old methods*).

1*st process.*—Evaporate the urine to dryness; mix the residue with sand, and distil. The silica liberates the phosphoric acid, which the carbon reduces. (Boyle and Hankwitz.)

2*nd process.*—Precipitate the urine with plumbic acetate; mix the precipitate with one-fourth its weight of charcoal, and distil. (Grobert.)

(2.) *Preparation from native calcic phosphate* (*such as sombrerite*) *and from bones.* (Process of Scheele modified by Vauquelin, Nicholas, etc.)

(*α.*) Bones (from which the gelatine may have been previously extracted) are heated in an open fire to whiteness, whereby "bone-earth" Ca_32PO_4 is obtained.

(*β.*) Three parts of this bone-earth are now digested for several days with a mixture of 2 parts of strong sulphuric acid (Sp. Gr. 1·55), and 18 to 20 parts of water. An insoluble sulphate of lime and a soluble monocalcic salt called "superphosphate" are thus formed :—

$$Ca_32PO_4 + 2H_2SO_4 = 2CaSO_4 + Ca2H_2PO_4.$$

Tricalcic phosphate (bone ash) + Sulphuric acid = Calcic sulphate + Calcic superphosphate.

(*γ.*) The mixture is now filtered through horsehair to remove the insoluble calcic sulphate.

(*δ.*) The clear filtrate is now evaporated to a syrup, which is then mixed with one-fourth its weight of charcoal and heated, whereby water is expelled, and an intimate mixture of charcoal and metaphosphate of lime formed :—

$$Ca2H_2PO_4 = Ca2PO_3 + 2H_2O.$$

Calcic superphosphate = Calcic metaphosphate + Water.

(*ε.*) This mixture is now distilled at a red heat in an earthenware retort rendered air-tight with borax and sandy clay, when phosphorus passes over and is collected under hot water :—

$$3(Ca2PO_3) + 10C = Ca_32PO_4 + 10CO + P_4.$$

Calcic metaphosphate + Carbon = Tricalcic phosphate + Carbonic oxide + Phosphorus.

[Wöhler recommends using sand and charcoal, whereby the whole of the phosphorus may be obtained. $2(Ca2PO_3) + 10C + 2SiO_2 = 2CaSiO_3 + 10CO + P_4$)].

(*ζ.*) The phosphorus is purified first by washing under hot water containing bleaching powder; then by fusion under ammonia to remove *acid impurities*, and finally under a mixture of sulphuric acid and potassic dichromate, whereby any *suboxide of phosphorus* present is oxidized and changed into soluble phosphoric acid. The pure phosphorus is then strained through leather under hot water, and cast into sticks.

(3.) Phosphorus may be prepared (although as a manufacturing process this has not been successful) by passing a stream of hydrochloric acid gas over a mixture of charcoal and heated bone ash (Cary-Montrand) :—

$$Ca_3 2PO_4 + 6HCl + 8C = 3CaCl_2 + 8CO + 3H_2 + P_2.$$

Tricalcic phosphate + Hydrochloric acid + Carbon = Calcic chloride + Carbonic oxide + Hydrogen + Phosphorus.

Varieties.—Phosphorus assumes different allotropic forms, of which, amongst others, are the following :—

1. *Clear transparent variety.*—This is a yellow, soft, wax-like body, tasteless in the solid form, but having a sharp, pungent flavour in solution. It has the odor of garlic. Its specific gravity varies from 1·838 to 1·853. It is a non-conductor of heat and electricity. It fuses at 111·2° F. (44° C.), the fumes in a dark room appearing luminous. Its specific heat between 36° and 13° C. is 0·202.

2. *White opaque variety* (Rose).—This is formed by the action of light and probably of oxygen on the above, when kept under water. The white opaque crust forms most readily when the water contains an abundance of calcareous matter. It may be, however, and probably is, some form of oxide rather than an allotrope. Specific gravity 1·515.

3. *Black variety* (Thénard) is said to be produced when the common phosphorus is melted and suddenly cooled to 32° F. (0° C.). Probably this form only results from some metallic impurity in the phosphorus employed.

4. *Red variety* (Schrötter, 1845) is formed by heating yellow phosphorus for thirty or forty hours in an atmosphere in which it cannot oxidise, at a temperature of from 460° to 478° F. (238° to 248° C.), or under pressure at 572° F. (300° C.). It is also formed when the yellow phosphorus (100 parts) is heated with *a little* iodine (1 part) or selenium, the excess of phosphorus (*i.e.* the quantity not needed by the iodine or selenium) instantly becoming amorphous.

In the manufacture of red phosphorus close iron vessels are used, the oxygen soon becoming exhausted by the combustion of a little of the phosphorus. The temperature under ordinary pressure must not exceed 500° F. (260° C.), or ordinary yellow phosphorus will be re-formed from the red allotrope. It may be purified from yellow phosphorus by the solvent action of CS_2, or by boiling with caustic soda. It is amorphous, and of a dull red color, without taste, odor, or action on the body. Its specific gravity is 2·14, and it fuses at 550·4° F. (288° C.). It conducts electricity feebly. It is not luminous until heated to its firing point 600·8° F. (316° C.). It is insoluble both in carbon bisulphide, and in sulphur chloride. It is changed back again to the common yellow variety by the action of a heat of 500° F. (260° C.), the change being accompanied by the evolution of great heat. If the heat be applied out of contact with air, the yellow phosphorus formed has the same weight as the original red phosphorus. It is permanent in the air, and gives off no vapor. It is not fired by contact with iodine.

Properties.—(*a.*) SENSIBLE.—A solid. The yellow variety may be prepared in octahedral or dodecahedral crystals by evaporating its solution in carbon disulphide in an atmosphere of carbonic anhydride. The red variety is amorphous. The *color* varies. The common variety is yellow; Rose's, white, like porcelain; Thénard's, black; and Schrötter's, red. The *odor* of all the varieties, excepting that of Schrötter, is said to be like garlic. Its *taste*, except Schrötter's variety, is acrid.

(β.) PHYSIOLOGICAL.—All varieties (except the red phosphorus) are active poisons, less than half a grain having proved fatal. Its exact physiological action is doubtful, some considering that its poisonous action is due to its oxidation internally at the expense of the oxygen of the blood; whilst others hold that it is a true blood poison, and remains unaltered by absorption. To remove it from the system by the stomach-pump, or, if after an interval, by an emetic, administering at the same time some thick gruel containing chalk or magnesia, the former to suspend the particles, and the latter to neutralise any acid products formed, constitutes the best method of treatment in cases of phosphorus poisoning. Above all, the administration of oil or fatty matter must be avoided. The red variety is not poisonous. The vapors, when inhaled (as in lucifer-match making), are liable to produce disease of the jaw bone.

(γ.) PHYSICAL.—*Specific Gravity.*—This varies: the specific gravity of the *yellow* variety ranges from 1·848 to 1·853; that of the *white* is 1·515; and of the *red*, 2·14. The *specific gravity of the vapor* is 4·303; that is, its volume is 62 times the weight of the same volume of hydrogen at the same temperature and pressure. Theoretically, it should be only 31 times the weight. The atom, therefore, must be regarded as one-half the size of the hydrogen atom, and the molecule as consisting of four atoms (P_4).

Action of Heat.—The yellow variety melts and fires at about 112° F. (44·6° C.). It may be cooled to 90° F. (32° C.) without solidifying, more particularly if it be melted under a solution of potassic hydrate; but if, whilst in this state of liquidity, it be touched under the solution with a solid point, it immediately solidifies, the temperature rising to 112° F. (44·5° C.). It volatilizes at ordinary temperatures in moist air, and at 217° F. (103° C.) in dry air, the vapor possessing an alliaceous odor. It boils or distils at 554° F. (290° C.), but when boiled in water, phosphorus vapor comes over along with the steam at 212° F. (100° C.). Above 1904° F. (1040° C.) however the vapor density indicates that the molecule of P_4 undergoes partial dissociation (Victor Meyer).

If the yellow variety be heated a little *above* its melting point, and suddenly cooled, it forms the black or Thénard's phosphorus; this variety may, however, be changed back again to the yellow form by fusion and slow boiling. If the yellow variety be heated *nearly*, but not quite, to its boiling point, and suddenly cooled, it becomes viscous. If the yellow phosphorus be heated for a long time at from 460° F.

(238° C.), to 480° F. (249° C.), in hydrogen, or in nitrogen, or in any atmosphere in which it cannot fire, it forms the red variety, or "Schrötter's phosphorus," which by a heat of 500° F. (260° C.) may be again reconverted into the yellow variety. Rose's, or the white phosphorus, at a heat of 122° F. (50° C.), becomes the ordinary yellow variety.

Action of Light.—When yellow phosphorus is exposed under water to *diffuse daylight,* a white covering is formed upon it (Rose's). *Sunlight* acting on yellow phosphorus, preserved either under water or in a vacuum, changes it to an orange-yellow. (Napoli.)

Action of Electricity.—Phosphorus is a bad conductor of electricity, unless it be melted.

When the hydrogen flame containing phosphorus is examined by the spectroscope, two green lines are apparent, one corresponding with one of the barium lines.

SOLUBILITY.—The solubility of phosphorus in different liquids is represented in the following table :—

Solubility of Phosphorus in various Liquids.

Water	Slight.
Strong Acetic acid	0·04 per cent.
Alcohol (Sp. Gr. 834)	0·4 ,,
Ether (Sp. Gr. 758)	0·9 ,,
Olive oil (Sp. Gr. 916	1·0 ,,
Turpentine (Sp. Gr. 996)	2·5 ,,
Carbon Bisulphide	10 to 15 times its weight.

The solutions, however, differ in strength very materially, according to the length of time that the solvent has been acting.

Table showing the Solubility of Phosphorus in various Liquids after remaining in contact with them for different times.

Liquid.	Quantity by Measure of Solvent.	Quantity by Weight of Phosphorus	Amount of Phosphorus taken up during					
			1st day.	2nd day.	3rd day.	4th day.	5th day.	6th day.
Alcohol	1 oz. =	400 grs.	0·31	0·42	0·54	0·96	1·5	1·6
Ether	1 oz. =	364 ,,	2·9	3·0	3·1	3·3	3·3	3·3
Olive Oil	1 oz. =	440 ,,	1·0	1·3	2·4	3·0	4·0	4·4
Turpentine	1 oz. =	478 ,,	3·1	4·8	6·5	8·6	10·0	12·0

(δ.) CHEMICAL.—Our remarks, for the present, refer to the ordinary yellow variety only. Phosphorus has an intense affinity for oxygen, acting therefore as a powerful reducing agent. *Phosphoric acid* is produced by its rapid combustion, and *phosphorous acid* by its slow combustion, in dry air or oxygen. (*See* Analysis of Air, p. 97.) In moist air the fumes evolved from phosphorus are luminous in the dark. They are said to consist of ammonic nitrate, formed by the action of ozonised oxygen on the air in the presence of aqueous vapor.

This slow combustion of phosphorus is influenced by many circumstances :

(1.) Phosphorus is not luminous in pure oxygen at a temperature below 60° F. (15·6° C.). Chappuis supposes the luminosity to depend on the presence of ozone in the air.

(2.) The presence of a diluting gas, such as hydrogen, nitrogen, etc., greatly reduces the temperature at which phosphorus becomes luminous.

(3.) It is essential that moisture should be present.

(4.) The luminosity is greatly promoted by heat, and checked by cold. It is not luminous in air at 32° F. (0° C.), and but faintly luminous at from 41° to 43° F. (5° to 6° C.) ; but above this the luminosity is in direct ratio to the temperature.

(5.) The luminosity is increased by rarefaction, whilst on the contrary, a pressure of four atmospheres entirely checks it.

(6.) The luminosity is stopped by the presence of certain gases and vapors. In addition to those mentioned in the following table, we may also name bromine, iodine, nitrous oxide, nitric oxide, vapors of alcohol and of the volatile oils, etc., as interfering with its slow combustion.[*]

Proportions in which certain Gases stop the slow Combustion of Phosphorus in Air at ordinary Temperatures and Pressures.

Name of the Gas.	Proportions in the air by volume.	Temperature when the luminosity ceases.	
		F.	C.
Sulphuretted hydrogen..	$\frac{1}{5}$	66·0	18·9
Sulphurous acid	$\frac{1}{11}$	44·9	7·2
Chlorine	$\frac{1}{12}$	53·9	12·2
Do.	$\frac{1}{25}$	65·8	18·8
Ether	$\frac{1}{150}$	65·8	18·8
Olefiant gas	$\frac{1}{450}$	65·8	18·8
Phosphoretted hydrogen	$\frac{1}{1000}$	65·8	18·8
Naphtha	$\frac{1}{1820}$	65·8	18·8
Oil of turpentine	$\frac{1}{4444}$	65·8	18·8
Bisulphide of carbon	Merest trace.	97·0	36·1

Quantities of Vapor required to check the Luminosity of Phosphorus in Air at elevated Temperatures.

Gas, or Vapor.	Proportions in the air by volume.	Temperature at which Oxidation ceases.	
		F.	C.
Olefiant gas	$\frac{1}{2}$	199·9	93·3
Ether	$\frac{1}{2}$	214·1	101·2
Do.	$\frac{2}{3}$	219·9	104·4
Naphtha	$\frac{1}{112}$[*]	169·8	76·6
Turpentine	$\frac{1}{156}$[*]	185·9	85·5

[*] With a large amount of naphtha and turpentine, phosphorus may be distilled without firing.

The oxidation of phosphorus in air, at ordinary temperatures, may be so rapid as to effect combustion, more particularly if the phosphorus be in a finely divided state. We may note that phosphorus flames do not spread, owing to the phosphoric acid generated as the product of combustion, collecting on neighbouring objects. Phosphorus combines with nascent hydrogen to form phosphoretted hydrogen.

Action of Water.—Phosphorus does not form a hydrate with water, but when preserved for some time under water, phosphorous acid and phosphoretted hydrogen are produced ($P_2+3H_2O=H_3PO_3+PH_3$).

Action of Haloids.—The haloids attack phosphorus instantly. If iodine and phosphorus be brought into contact, they at once ignite. Brodie has shown that if a little iodine be added to yellow phosphorus, melted in an atmosphere of carbonic anhydride, it will convert an almost unlimited quantity of the yellow into the red amorphous variety. This result depends on the formation of an iodide of phosphorus, the phosphorus of which compound is amorphous. This iodide is decomposed as soon as formed by the yellow phosphorus to make more iodide, which is again decomposed, the action proceeding indefinitely, until the whole of the yellow is converted into the red allotrope.

Phosphorus combines *with sulphur, selenium,* and *the metals* (gold and platinum not excepted) when heated with them. A platinum dish, if constantly used for igniting organic substances containing phosphates, becomes rough. The presence of phosphorus in iron or copper, effects considerable alteration in their properties.

Action on Metallic Solutions.—Phosphorus reduces the salts of many of the metals, such as those of gold, silver, copper, platinum, etc., but it has no action on the salts of lead, iron, zinc, antimony, arsenic or manganese.

Action of Acids.—Hydrochloric acid, hot or cold, has no action on phosphorus. *Sulphuric acid* in the cold has no action on phosphorus, but when heated with it the acid is decomposed ($3H_2SO_4+P_2=2H_3PO_3$ (*phosphorous acid*) $+3SO_2$). *Sulphurous acid* is also decomposed by it. *Nitric acid* oxidises it with the formation of phosphoric acid and the evolution of the lower nitrogen oxides ($6HNO_3+P_2=2H_3PO_4$(*phosphoric acid*) $+2N_2O_4+2NO$).

Action of Alkalies and Alkaline Earths.—When phosphorus is heated in contact with the alkalies and alkaline earths, it forms alkaline or earthy hypophosphites, phosphides, phosphates, etc. If the vapor of phosphorus be passed over lime heated to redness, a chocolate red powder (a mixture of calcic phosphide and calcic pyrophosphate) is formed :—

$$\underset{\text{Phosphorus}}{14P} + \underset{\text{Lime}}{14CaO} = \underset{\text{Calcic pyrophosphate}}{2Ca_2P_2O_7} + \underset{\text{Calcic phosphide.}}{5Ca_2P_2}$$

If phosphorus be boiled with caustic soda or potash, phosphoretted hydrogen is evolved, and a hypophosphite is formed :—

$$3KHO + P_4 + 3H_2O = 3KH_2PO_2 + PH_3$$

Potassic hydrate + Phosphorus + Water = Potassic hypophosphite + Phosphoretted hydrogen.

Heated to redness with sodic carbonate, phosphorus effects a reduction of the carbonic anhydride, whereby carbon is liberated.

Phosphorus has no action on dead mucous membrane, unless both be freely exposed to the air, when the phosphorus softens, discolors, and in time dissolves the tissue.

The red variety is not characterised by any of the reactions already described. It is singularly negative in its chemical properties.

Tests.—1. *Odor.*—This may be recognised in very dilute solutions.

2. *Property of Fuming in the Air and Shining in the Dark.*—These effects are only manifest when the phosphorus is examined either in the dry state, or in solution in water, vinegar, or in the fixed oils, the luminosity being intensified by the application of heat. It is not manifested when it is dissolved in ether, carbon disulphide, alcohol, turpentine, or in the volatile oils, until the solvent has completely evaporated.

3. *Faculty of Evolving Ozone, etc., in Damp Air.*—This may be known by—

(α.) A solution of argentic nitrate becoming black.
(β.) Starch and potassic iodide becoming blue.
(γ.) Litmus paper being first reddened and afterwards bleached.
(δ.) The protosalts of manganese being discolored.

4. *Color of the Flame and the Products of Combustion.*

5. *Action on certain Metallic Compounds:* —

(α.) Solid phosphorus reduces metallic gold, silver, copper, etc., from solutions of their salts.

(β.) *Argentic Nitrate* gives a black precipitate with a solution of phosphorus; *cupric* sulphate, a brown precipitate; and *mercuric chloride*, a *yellow* precipitate.

6. *Conversion into Phosphoric Acid.* Boil the phosphorus in a retort with twelve or fourteen times its weight of dilute nitric acid (Sp. Gr. 1·200). Evaporate the solution nearly to dryness, and dissolve the residual phosphoric acid in water. To this solution the tests proper to phosphoric acid must be applied.

Uses.—*In Nature* phosphorus appears essential to animal and vegetable life. It is found abundantly in brain tissue, and more particularly in the sexual organs of both plants and animals. *In the Arts* its principal use is for lucifer matches. The wood is tipped either with sulphur or with paraffin to render it easy of ignition, and afterwards with a phosphorus composition, in which case the phosphorus is usually mixed with nitre on the Continent (silent matches), and with potassic chlorate in England (detonating matches). The use of safety matches, where red phosphorus is employed, is becoming extensive. The matches are tipped with a mixture of chlorate and bichromate of potash, red lead, and sulphide of antimony, whilst the paper on which they have to be rubbed is coated with a mixture of sulphide of antimony and amorphous phosphorus. It is evident from their composition that with great friction it would be possible to ignite one of these matches on an unprepared surface. *In Medicine* phosphorus acts as a nervine tonic and aphrodisiac. It is given in skin diseases, low fevers, phthisis, etc. *Oleum Phosphoratum,* B.P., 12 grs. in 4 fluid ounces of dried almond oil; *Pilula Phosphori,* B.P., phosphorus in balsam of tolu and yellow wax.

COMPOUNDS OF PHOSPHORUS AND OXYGEN.

Oxides or Anhydrides.	Formula.	+ Water^n	= Acids of Phosphorus.	Name of Acids.
Suboxide of phosphorus	P_4O (?)			
——	——	——	—— H_3PO_2	Hypophosphorous.
Phosphorous anhydride	P_2O_3	$+3H_2O$	$= H_6P_2O_6$ (H_3PO_3)	Phosphorous.
Phosphoric anhydride	P_2O_5	$+ H_2O$	$= 2HPO_3$ (HPO_3)	Metaphosphoric.
Do.	do.	$+2H_2O$	$= H_4P_2O_7$	Pyrophosphoric.
Do.	do.	$+3H_2O$	$= 2H_3PO_4$ (H_3PO_4)	Orthophosphoric.
*	$2P_2O_5$	$+3H_2O$	$= H_6P_4O_{13}$	Hexabasic Phosphoric.
	$5P_2O_5$	$+6H_2O$	$= H_{12}P_{10}O_{31}$	Dodecabasic Phosphoric.
			$H_8P_4O_{12}$	Hypophosphoric.

It will be noted from the above table—

1. That there is no anhydride of hypophosphorous acid.

2. That, omitting the last three acids, of which we know very little, phosphoric anhydride forms three acids by combination with 1, 2, and 3 molecules of water respectively.

3. That hypophosphorous acid (H_3PO_2), phosphorous acid (H_3PO_3), and orthophosphoric acid (H_3PO_4) respectively contain 3 atoms of hydrogen in the molecule, but that they differ as follows :—

(*a*) *Hypophosphorous acid* is Monobasic, *i.e.*, only 1 hydrogen can be [replaced by a metal.
(*β*) *Phosphorous acid* is Dibasic, *i.e.*, 2 hydrogens ditto
(*γ*) *Phosphoric acid* is Tribasic, *i.e.*, 3 ditto ditto

Suboxide of Phosphorus (P_4O) ?

This compound is supposed to constitute a portion of the colored residue left after the combustion of phosphorus in air. This deposit is generally regarded as a mixture of red phosphorus with a little phosphoric acid. It is also said to be formed by acting on phosphorus with phosphorous chloride, exposing the mixture to air, and afterwards boiling the mass in water.

---

* These three acids are said to exist, but our knowledge of them is very imperfect.

Hypophosphorous Acid, $H_3PO_2=66$.

The anhydride of this acid has never been obtained.

Preparation.—(1.) By decomposing baric hypophosphite with sulphuric acid :—(*a.*) A baric hypophosphite is first prepared by boiling phosphorus in a solution of baric hydrate (Rose) :—

$$3BaH_2O_2 + 2P_4 + 6H_2O = 3(Ba,2H_2PO_2) + 2H_3P.$$

Baric hydrate + Phosphorus + Water = Baric hypophosphite + Phosphoretted hydrogen.

(*β.*) The insoluble baric hypophosphite is then decomposed with sulphuric acid, hypophosphorous acid being set free :—

$$3(Ba2H_2PO_2) + 3H_2SO_4 = 3BaSO_4 + 6H_3PO_2.$$

Baric hypophosphite + Sulphuric acid = Baric sulphate + Hypophosphorous acid.

2. By decomposing lead hypophosphite with sulphuretted hydrogen :—

$$(Pb2H_2PO_2) + H_2S = PbS + 2H_3PO_2.$$

Plumbic hypophosphite + Sulphuretted hydrogen = Plumbic sulphide + Hypophosphorous acid.

Properties.—Hypophosphorous acid may be obtained as a thick viscid liquid by careful evaporation under the receiver of an air-pump, yielding crystals on cooling to 32° F. (0° C.). The crystals fuse at 67·3° F. (17·4° C.). The acid has a strong acid reaction. When heated it is decomposed, yielding phosphoric acid and phosphoretted hydrogen ($2H_3PO_2=H_3PO_4+H_3P$). It rapidly oxidizes by exposure to air, forming phosphoric acid ($H_3PO_2+O_2=H_3PO_4$). It acts as a powerful reducing agent on salts of gold, mercury, etc.

Hypophosphorous acid may be known from phosphorous acid by adding cupric sulphate to the free acid and heating the solution to 131° F. (55° C.). With *hypophosphorous acid* a reddish black precipitate of cupric hydride (Cu_2H_2) is thrown down, which, when heated in the liquid to 212° F. (100° C.), is decomposed with the deposition of the metal and the evolution of hydrogen, whilst with *phosphorous acid*, the metal is precipitated and hydrogen evolved, but no Cu_2H_2 is formed. Further, hypophosphorous acid reduces the permanganates immediately, but phosphorous acid only after some time. When hypophosphorous acid is treated with zinc and sulphuric acid, it is converted into phosphoretted hydrogen.

Although the acid contains three atoms of hydrogen, it is nevertheless monobasic. Thus it forms salts as follows :—

(*a.*) Salts of monad metals — *e.g.*, $K'H_2PO_2$.
(*β.*) Salts of dyad metals — *e.g.*, $Ba'' 2(H_2PO_2)$.

These salts are prepared by boiling phosphorus in an alkaline solution—

(α.) $3HKO + P_4 + 3H_2O = 3(KH_2PO_2) + H_3P$;
(β.) $3BaO + 2P_4 + 9H_2O = 3(Ba2H_2PO_2) + 2H_3P$.

The hypophosphites are used in medicine, as *e.g.*, *Calcis hypophosphis*, B.P. (Prep. : by boiling together lime, phosphorus, and water) ; and *Sodæ hypophosphis*, B.P. They are commonly used in the form of syrups.

Phosphorous Anhydride, P_2O_3=110.

Synonyms.—*Phosphorous Trioxide ; Phosphorous Oxide.*

Preparation.—(1.) By the slow combustion of phosphorus in dry air or in oxygen.

(2.) By burning phosphorus in a very limited supply of air.

Properties.—There is some doubt whether this body is truly phosphorous anhydride. For if it be allowed to deliquesce, air being excluded, a *neutral* solution is obtained which does not dialyse, pointing to a higher molecular weight. By applying heat to this liquid, however, a solution containing H_3PO_3 is formed, a reddish substance separating.

Prepared as directed, phosphorous anhydride is a white, flaky, non-crystalline, inflammable solid, very volatile, emitting a garlic-like odor. It is highly deliquescent, heat being evolved by its combination with water with the formation of phosphorous acid. Phosphorous acid cannot be changed back to phosphorous anhydride by heat. If phosphorous anhydride be heated in a sealed tube, phosphoric anhydride and free phosphorus are formed ($5P_2O_3 = 3P_2O_5 + P_4$.)

Phosphorous Acid, H_3PO_3=82.

Synonym.—*Hydric Phosphite.*

Preparation. — (1.) By the action of water on the phosphorous anhydride (P_2O_3) last described.

(2.) By passing moist air over phosphorus.

(3.) By the action of chlorine on melted phosphorus under hot water. A phosphorous chloride is first formed, which is afterwards decomposed by the water. Thus—

(α.) $P_2 + 3Cl_2 = 2PCl_3$.
Phosphorus + Chlorine = Phosphorous chloride.

(β.) $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$.
Phosphorous chloride + Water = Phosphorous acid + Hydrochloric acid.

(4.) By the action of a saturated solution of cupric sulphate on phosphorus, whereby an insoluble copper phosphide is formed, phosphorous and sulphuric acids remaining in solution. The removal of the H_2SO_4 is effected by precipitation with baryta water.

(5.) By heating phosphorus chloride with crystallised oxalic acid.

Properties. (*a.*) *Sensible and Physical.*—A thick syrupy liquid, from which deliquescent crystals, fusing at 158° F. (70° C.) may be obtained. It is decomposed by a heat of 372° F. (180° C.) into phosphoric acid and phosphoretted hydrogen ($4H_3PO_3=3H_3PO_4+PH_3$).

(*β.*) *Chemical.*—Its affinity for oxygen renders it a powerful reducing agent. Thus, when phosphorous acid is exposed to the air, phosphoric acid is formed. By the action of phosphorous acid on the salts of silver, gold, etc., the metal is reduced. It does not reduce copper salts. With mercuric chloride it first precipitates calomel. It reduces sulphurous acid, free sulphur being deposited by the secondary action of the H_2S on the SO_2 ($2SO_2+2H_2O+6H_3PO_3=2H_2S+6H_3PO_4$).

Phosphorous acid is a tribasic acid. Thus it is tribasic in the phosphorous ethers, where, as in triethyl phosphorous acid $(C_2H_5)_3PO_3$, all three hydrogens of the acid are replaced by alcohol radicals, although only two of the radicals of these compounds can be replaced by metals M′, the mono- and dibasic salts being the only ones that are stable. Thus, inasmuch as one or two hydrogen atoms only of the acid are capable of substitution by a metal, it is more accurate to regard it as dibasic. Thus—

Salts (with monads)	Acid $M'H_2PO_3$ as KH_2PO_3. Normal M_2HPO_3 as K_2HPO_3.
Other salts (with dyads)	Acid $M''(H_2PO_3)_2$. Normal $M''HPO_3$.

To distinguish phosphorous from hypophosphorous acid, *see* page 159.

Phosphoric Anhydride ($P_2O_5=142$).

Preparation.—By burning phosphorus in oxygen or in dry air. Note.—It *cannot* be prepared by the action of heat on hydrated hosphoric acid.]

Properties.—Phosphoric anhydride is a white, flaky, deliquescent olid, fusible and volatile at a red heat, subliming unchanged. It isses when thrown into water, metaphosphoric acid (HPO_3) being ormed. The water which thus enters into combination cannot be gain completely expelled by heat. It is the most powerful desiccating gent known. Heated with carbon, it yields carbonic oxide and phoshorus.

Phosphoric anhydride combines with one, two, or three molecules f water, forming three acids as follows :—

(1.) $P_2O_5+H_2O=2HPO_3$ =metaphosphoric acid.
(2.) $P_2O_5+2H_2O=H_4P_2O_7$ =pyrophosphoric acid.
(3.) $P_2O_5+3H_2O=2H_3PO_4$ =ortho- or common phosphoric acid.

Metaphosphoric Acid ($HPO_3=80$).

Synonyms. — *Hydric metaphosphate; Monohydrogen phosphate* oscoe) ; *Glacial phosphoric acid; Monobasic phosphoric acid.*

Preparation.—(1.) By dissolving phosphoric anhydride in cold water ($P_2O_5+H_2O=2HPO_3$).

(2.) By the action of heat on ortho- or tribasic phosphoric acid, whereby glacial metaphosphoric acid is formed ($H_3PO_4=H_2O+HPO_3$).

Properties.—A colorless fusible solid, very soluble in water. The acid in solution changes to orthophosphoric acid by attracting water, the conversion being slow at ordinary temperatures, but rapid when boiled.

Metaphosphoric acid is monabasic and therefore forms one series of salts only.

The metaphosphates are formed by the action of heat either on a *dihydric phosphate* of a fixed base ($NaH_2PO_4=NaPO_3+H_2O$), or on a *monohydric phosphate* containing one atom of a volatile base ($NH_4NaHPO_4=NH_3+H_2O+NaPO_3$), or on a *dihydric pyrophosphate* ($Na_2H_2P_2O_7=H_2O+2NaPO_3$).

Tests.—(1.) *Argentic Nitrate*, a white precipitate ($AgPO_3$).

(2.) The acid coagulates albumen.

Pyrophosphoric Acid ($H_4P_2O_7=178$).

Synonyms.—*Tetrahydric pyrophosphate; Hydrogen pyrophosphate* (Roscoe). *Diphosphoric acid.*

Preparation.—(1.) By heating orthophosphoric acid to 419° F. (215° C.) ($2H_3PO_4=H_2O+H_4P_2O_7$).

(2.) By decomposing plumbic pyrophosphate ($Pb_2P_2O_7$) with sulphuretted hydrogen :—

$$\underset{\text{Plumbic pyrophosphate}}{Pb_2P_2O_7} + \underset{\text{Sulphuretted hydrogen}}{2H_2S} = \underset{\text{Plumbic sulphide}}{2PbS} + \underset{\text{Pyrophosphoric acid.}}{H_4P_2O_7.}$$

[Plumbic pyrophosphate may be prepared by heating the rhombic crystals of common sodic phosphate ($Na_2HPO_4+12H_2O$), when anhydrous sodic phosphate (Na_2HPO_4) is first formed, becoming by further heat sodic pyrophosphate ($Na_4P_2O_7$). This change results from a combination of two molecules of Na_2HPO_4, and the expulsion therefrom of one molecule of water.

$$\underset{\text{Common sodic phosphate}}{2Na_2HPO_4} = \underset{\text{Sodic pyrophosphate}}{Na_4P_2O_7} + \underset{\text{Water.}}{H_2O.}$$

On dissolving the sodic pyrophosphate thus formed in water, and adding plumbic acetate, a plumbic pyrophosphate will be precipitated ($Pb_2P_2O_7$).]

Properties.—Pyrophosphoric acid solution evaporated '*in vacuo*' over sulphuric acid deposits crystals. It does not coagulate albumen. In solution, it becomes the tribasic acid (slowly at ordinary temperatures, but rapidly if heated) by absorbing water.

It is a tetrabasic acid. Thus in the sodium salt, we may have all the hydrogens substituted by the metal.

Tests.—(1.) *Calcic or baric salts;* a white precipitate.

(2.) *Argentic nitrate:* a white precipitate ($Ag_4P_2O_7$). If the original solution be neutral, it will remain neutral after the nitrate of silver has been added, no free acid being liberated.

Phosphoric Acid (H_3PO_4=98).

Synonyms.—*Orthophosphoric acid; Tribasic phosphoric acid; Common phosphoric acid; Trihydric phosphate; Hydric phosphate.*

Natural History.—(α.) In the *animal* kingdom, orthophosphoric acid is found largely in bones, and in *guano*, which is the partially lecomposed excrement of sea fowl, and in all parts of the animal as well as in all excretions and secretions. (β.) In *vegetables* it is an ssential principle, "superphosphate" constituting one of their most valuable foods. (γ.) In the *mineral* kingdom it is found as phoshorite, apatite, coprolite (named under the notion that it was etrified dung), wavellite, pyromorphite, etc. In all cases, however, it s found in combination, and chiefly with lime and magnesia.

Preparation.—(1.) By dissolving phosphoric anhydride (P_2O_5) in vater, and boiling the solution.

(2.) By boiling meta- or pyro-phosphoric acid in water.

(3.) By boiling phosphorus with dilute nitric acid, the lower nitroen oxides being evolved. (This is the method of preparing acid hosphoricum dilutum, B.P., Sp. Gr. 1·08=10 per cent. of P_2O_5.)

(4.) By the combustion of phosphoretted hydrogen in air or oxygen $PH_3+2O_2=H_3PO_4$).

(5.) By decomposing the triplumbic phosphate with sulphuretted ydrogen ($Pb_32PO_4+3H_2S=2H_3PO_4+3PbS$).

(6.) By the action of water on phosphoric chloride.

(7.) *Commercial Process.*—By decomposing bone-ash ($Ca_3P_2O_8$) with rong sulphuric acid, removing the insoluble calcic sulphate, decomsing the residual acid calcic phosphate with carbonate of ammonia, tering to separate the calcic carbonate, evaporating to dryness, niting to get rid of ammonia and water, redissolving the residue, and iling.

Properties.—Tribasic or common phosphoric acid is a syrupy and ry acid liquid. By evaporation "in vacuo" it may be obtained in nsparent prisms, which deliquesce in the air and fuse at 101·4° F. 8·6° C.). By a heat of 329° to 410° F. (160° to 210° C.), it loses ter and forms *pyro*phosphoric acid ($2H_3PO_4=H_4P_2O_7+H_2O$), nich, at a red heat, becomes glacial *meta*phosphoric acid ($H_4P_2O_7=$ $O+2HPO_3$).

Orthophosphoric acid is the phosphoric acid of common phosphates. It is tribasic, and forms three classes of salts by the substitution of 1, 2, or 3 hydrogens by a metal. Thus,

1. Acid Salts { $M'H_2PO_4$ or $M''2H_2PO_4$, as $Na'H_2PO_4$, dihydric sodic phosphate (superphosphates).
$M'_2H.PO_4$ or M''_22HPO_4, as Na'_2HPO_4, common sodic phosphate.
2. Normal Salt M'_3PO_4 or M''_32PO_4, as Na'_3PO_4 trisodic phosphate.

When these salts are heated, they lose water and form other salts. Further, the base need not be necessarily confined to one metal; thus, in microcosmic salt (the sodic-ammonic hydric phosphate for example, $NaNH_4HPO_4,4H_2O$), we have three different basyls in one compound.

Tests.—*Reactions of ortho- or common phosphoric acid.*

(*a.*) *In a free or combined state in an acid solution*:—

(1.) *Ammonic molybdate*, a yellow precipitate, when heated, of ammonic molybdophosphate, soluble in ammonia.

(*b.*) *In a combined state*:—

(1.) *Lime* or *baryta water*, a white precipitate.

(2.) *Ammonia* and *magnesic sulphate*, a white precipitate:—($Mg''NH_4PO_4,6H_2O$), insoluble in ammonia, soluble in acids. This ignited becomes $Mg_2P_2O_7$.

(3.) *Argentic nitrate*, a yellow precipitate (Ag_3PO_4), the solution, although previously neutral, becoming acid. Soluble in ammonia and in nitric acid.

(4.) *Plumbic acetate* or *mercurous* or *bismuth nitrate*, white precipitates (Pb_32PO_4).

(5.) Whitish yellow precipitates, with *uranic nitrate* or *ferric chloride*, soluble in ammonia and in hydrochloric acid.

Uses.—*In nature* it plays an important part in animal and vegetable tissues.

In the arts it is used in calico printing, and *in medicine* its use is indicated in such diseases as rickets, etc.

[*Ammoniæ phosphas*, $(NH_4)_2HPO_4$, is made by adding ammonia to phosphoric acid, and allowing the crystals to form. *Calcis phosphas* (Ca_32PO_4) prepared from bones (os ustum, B.P.) as already described. *Sodæ phosphas* ($Na_2HPO_4,12H_2O$), prepared from the acid phosphate of calcium, by the addition of sodic carbonate ($Ca2H_2PO_4 + Na_2CO_3 = Na_2HPO_4 + H_2O + CO_2 + CaHPO_4$). *Ferri phosphas* ($Fe_32PO_4$) prepared by adding sodic phosphate and acetate to ferrous sulphate ($3FeSO_4 + 2Na_2HPO_4 + 2NaC_2H_3O_2 = Fe_32PO_4 + 3Na_2SO_4 + 2C_2H_4O_2$). *Acidum phosphoricum dilutum*, prepared by the action of nitric acid on phosphorus.]

GENERAL REMARKS ON THE ACIDS OF THE OXIDES OF PHOSPHORUS.

It will be convenient here to generalise on the acids of the oxides of phosphorus.

1. There are three modifications of phosphoric acid, viz. :—

(α.) Meta- or monohydric or monobasic phosphoric acid—HPO_3, or H_2O,P_2O_5.

(β.) Pyro- or tetrahydric or tetrabasic phosphoric acid—$H_4P_2O_7$, or $2H_2O,P_2O_5$.

(γ.) Ortho- or trihydric or tribasic phosphoric acid—H_3PO_4, or $3H_2O,P_2O_5$.

2. These acids may be severally prepared by passing sulphuretted hydrogen through water containing the corresponding silver or lead salt in suspension. Thus,

(α.)	$2AgPO_3$	+	H_2S	=	$2HPO_3$	+	Ag_2S.
	Argentic metaphosphate	+	Sulphuretted hydrogen	=	Metaphosphoric acid	+	Argentic sulphide.
(β.)	$Ag_4P_2O_7$	+	$2H_2S$	=	$H_4P_2O_7$	+	$2Ag_2S$.
	Argentic pyrophosphate	+	Sulphuretted hydrogen	=	Pyrophosphoric acid	+	Argentic sulphide.
(γ.)	$2Ag_3PO_4$	+	$3H_2S$	=	$2H_3PO_4$	+	$3Ag_2S$.
	Argentic Orthophosphate	+	Sulphuretted hydrogen	=	Orthophosphoric acid	+	Argentic sulphide.

3. (α.) The solution of P_2O_5 in cold water forms *Metaphosphoric acid*, HPO_3.

(β.) This solution (other hydrates being present) on boiling becomes *Pyrophosphoric acid*, $H_4P_2O_7$,

(γ.) Which on prolonged boiling yields *Orthophosphoric acid*, H_3PO_4.

4. These acids are distinguished from one another by their reactions on albumen, on argentic nitrate, and on baric nitrate as follows :—

	On Albumen.	On Argentic nitrate.	On Baric nitrate.
(α.) Metaphosphoric acid	Coagulates	White gelatinous ppt. ($AgPO_3$).	White ppt.
(β.) Pyrophosphoric acid	No action	No ppt. unless rendered alkaline, when it gives a *white* ppt. ($Ag_4P_2O_7$).	No ppt. unless alkaline, when it gives a white ppt.
(γ.) Orthophosphoric acid .	No action	No ppt. unless rendered alkaline, when it gives a *yellow* ppt. (Ag_3PO_4).	Ditto ditto.

5. These acids form corresponding salts as follows :—

(α.) *Metaphosphates*, or monophosphates—

$$M'PO_3 \quad \left\{ \begin{array}{l} Na'PO_3. \\ Pb''2PO_3. \end{array} \right.$$

(β.) *Pyrophosphates*, or tetraphosphates—

$$M'_4P_2O_7 \quad \left\{ \begin{array}{l} Na'_4P_2O_7+10H_2O. \\ Pb''_2P_2O_7. \end{array} \right.$$

(γ.) *Orthophosphates,* or triphosphates—

$$M'_3PO_4 \begin{cases} NaH_2PO_4,H_2O. \\ Na_2HPO_4,12H_2O. \\ Na_3PO_4,12H_2O. \\ NaNH_4HPO_4,4H_2O. \\ Ca_32PO_4. \\ Ca''H_42PO_4. \end{cases}$$

6. All forms of phosphates may be converted into tribasic phosphates by fusion with an alkaline hydrate or carbonate.

7. It will be noted that if water or ammonia (these being volatile) enter into the composition of the salts, heat will convert an orthophosphate into a pyrophosphate, and a pyrophosphate into a metaphosphate. This will be better seen as follows :—

(1.) *Disodic hydric orthophosphate* $(Na_2O)_2H_2O,P_2O_5$	when heated becomes	*Sodic pyrophosphate.* $(Na_2O)_2P_2O_5$.
(2.) *Sodic hydric pyrophosphate* Na_2O,H_2O,P_2O_5	,, ,,	*Sodic metaphosphate.* Na_2O,P_2O_5.
(3.) *Sodic ammonic hydric orthophosphate* $Na_2O,(NH_4)_2O,H_2O,P_2O_5$ (Microcosmic salt)	,, ,,	*Sodic metaphosphate.* Na_2O,P_2O_5.

8. The reaction of the several salts after the addition of argentic nitrate is important :—

(α.) A solution of metaphosphate of soda (Na_2O,P_2O_5 or $NaPO_3$) is slightly *acid.* On adding argentic nitrate, *a white gelatinous precipitate* is thrown down, and the solution becomes *neutral,* thus—

$$NaPO_3 + AgNO_3 = AgPO_3 + NaNO_3.$$

Sodic metaphosphate + Argentic nitrate = Argentic metaphosphate + Sodic nitrate.

(β.) A solution of sodic pyrophosphate ($2Na_2O,P_2O_5$, or $Na_4P_2O_7$) is *alkaline.* On adding argentic nitrate *a white precipitate* is thrown down, and the solution becomes *neutral.* Thus—

$$Na_4P_2O_7 + 4AgNO_3 = Ag_4P_2O_7 + 4NaNO_3.$$

Sodic pyrophosphate + Argentic nitrate = Argentic pyrophosphate + Sodic nitrate.

(γ.) A solution of sodic orthophosphate ($NaO,2H_2O,P_2O_5$ or Na_2HPO_4) is *alkaline.* On adding argentic nitrate *a yellow precipitate* is thrown down, and the solution becomes *acid.* Thus—

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$

Sodic orthophosphate + Argentic nitrate = Argentic orthophosphate + Sodic nitrate + Nitric acid.

9. Other varieties of phosphates have been described by Fleitmann and Henneberg :—

(α.) By heating together one molecule of sodic pyrophosphate and two of metaphosphate, a salt is obtained consisting of $2Na_3PO_4,P_2O_5$. (Sodium salt of hexabasic phosphoric acid, $H_6P_4O_{13}$).

(β.) By heating one molecule of pyrophosphate with eight of metaphosphate, a salt is obtained consisting of $4Na_3PO_4,3P_2O_5$. (Sodium salt of dodecabasic phosphoric acid, $H_{12}P_{10}O_{31}$).

Corresponding silver and magnesium compounds have been obtained.

These compounds are very unstable, quickly becoming mixtures of pyrophosphate and metaphosphate.

COMPOUNDS OF PHOSPHORUS WITH THE HALOIDS, &c.

With Chlorine.	With Bromine.	With Iodine.	With Fluorine.
——	——	Diiodide PI_2	——
Trichloride .. PCl_3	Tribromide .. PBr_3	Triiodide PI_3	——
Pentachloride PCl_5	Pentabromide PBr_5	——	Pentafluoride PF_5
Oxytrichloride $POCl_3$	Oxytribromide $POBr_3$	——	——
$P_2O_3Cl_4$	——	——	——
Sulphotrichloride .. .. $PSCl_3$	Sulphotribromide .. .. $PSBr_3$	——	——

Phosphorous Chloride, PCl_3.

Molecular weight, 137·6. *Molecular volume*, ☐☐. *Specific gravity of liquid*, 1·613 ; *of vapor*, 4·79. *Boils at* 168·8° F. (76° C.).

Synonyms.—*Trichloride or Terchloride of Phosphorus.*

Preparation. (1.) By passing phosphorus vapor over heated mercuric chloride (corrosive sublimate).

(2.) By the action of chlorine on dry melted phosphorus ($P_2+3Cl_2=2PCl_3$).

Properties.—A transparent colorless volatile liquid, soluble in benzol and in carbon disulphide. It dissolves phosphorus and absorbs chlorine freely, forming PCl_5. It does not solidify at —175° F. (—115° C.). At its boiling point, 165·2° F., (74° C.) it absorbs oxygen, forming $POCl_3$. It is decomposed by sulphuretted hydrogen ($PCl_3+3H_2S=6HCl+P_2S_3$) by alcohol, by ether, and by a large excess of water, in the latter case hydrochloric and phosphorous acids being produced. If hot water be used the re-action is very violent:—

$$\underset{\text{Phosphorous chloride}}{PCl_3} + \underset{\text{Water}}{3H_2O} = \underset{\text{Hydrochloric acid}}{3HCl} + \underset{\text{Phosphorous acid}}{H_3PO_3}.$$

Phosphoric Chloride, PCl_5.

Molecular weight, 208·5. *Molecular volume, below* 302° F. (150° C.) ☐☐ *Specific gravity of vapor at* 572° F. (300° C.), 3·654.

Synonyms.—*Pentachloride or Perchloride of Phosphorus.*

Preparation.—(1.) By the action of chlorine either on dry phosphorus in an exhausted flask, or on phosphorous chloride ($PCl_3+Cl_2=PCl_5$).

(2.) By passing chlorine through a solution, artificially cooled, of phosphorus in carbon disulphide. The solution is afterwards evaporated to dryness.

Properties.—A white deliquescent crystalline solid, volatile (before melting) at 212° F. (100° C.). At a temperature above 302° F. (105° C.) it dissociates into PCl_3 and Cl_2. Thus at high temperatures its vapor density is one-half that required by the formula PCl_5. It is worth recording that Wurtz determined the vapor density of PCl_5 by volatilising it in an atmosphere of PCl_3, by which means, to a great extent, he prevented dissociation. It may be fused under pressure at 298° F. (148° C.). It burns when passed into a flame, chlorine and phosphoric anhydride being formed. It combines with ammonia. It is decomposed by an excess of water, hydrochloric and phosphoric acids being formed :—

$$\begin{array}{ccccccccc} PCl_5 & + & 4H_2O & = & 5HCl & + & H_3PO_4. \\ \text{Phosphoric chloride} & + & \text{Water} & = & \text{Hydrochloric acid} & + & \text{Phosphoric acid.} \end{array}$$

In the laboratory it is largely used in the investigation of organic compounds on account of its power of effecting the substitution of Cl_2 in certain compounds for O.

When acted on with acids or with alcohols, chlorides of the radicals of the said alcohols and acids result. Thus $C_2H_5(HO)$ (*Ethylic Alcohol*) becomes C_2H_5Cl (*Ethylic Chloride*).

Phosphoric Oxychloride, $POCl_3$.

Molecular weight, 153·5. *Molecular volume,* ☐☐. *Specific gravity of liquid,* 1·7 ; *of vapor,* 5·298. *Boils at* 230° F. (110° C.).

Synonyms.—*Phosphoryl Chloride or Trichloride; Oxytrichloride of Phosphorus.*

Preparation.—(1.) By the slow action of a small quantity of water on phosphoric chloride ($PCl_5+H_2O=POCl_3+2HCl$).

(2.) By passing oxygen through boiling phosphorous chloride ($PCl_3+O=POCl_3$).

(3.) By heating together in a sealed tube phosphoric chloride and phosphoric anhydride ($3PCl_5+P_2O_5=5POCl_3$).

(4.) By heating oxidized compounds, such as an organic acid (oxalic or boric acid), with phosphoric chloride (Gerhardt) ($3PCl_5+2H_3BO_3=3POCl_3+6HCl+B_2O_3$).

Properties. A volatile, limpid, fuming liquid, solidifying at 14° F.

(-10° C.) boiling at 230° F. (110° C.), decomposed by water into hydrochloric and phosphoric acids ($POCl_3 + 3H_2O = H_3PO_4 + 3HCl$).

The importance of this compound, as well as of the other chlorides of phosphorus, depends on its action in producing various organic substitution products.

The body $P_2O_3Cl_4$ (*pyrophosphorylic chloride*) a fuming liquid having a sp. gr. of 1·58 has been described. It is prepared by passing nitric peroxide into phosphorous chloride. With water it forms phosphoric and hydrochloric acids, and with phosphoric chloride, the phosphoric oxychloride ($POCl_3$).

The bromides and oxybromide of phosphorus correspond in all respects to the chlorine compounds. $POBr_3$ boils at 383° F. (195° C.).

OTHER COMPOUNDS OF PHOSPHORUS AND THE HALOIDS.

The Biniodide of Phosphorus (PI_2) is prepared by adding 2 atoms of iodine to 1 atom of phosphorus dissolved in carbonic disulphide, and subsequently cooling the mixture. It forms orange-coloured prismatic crystals, melting at 230° F. (110° C.), and decomposed by water. It has no analogue amongst oxygen, chlorine, or bromine compounds.

Phosphorous bromide and iodide (PBr_3 and PI_3) are prepared similarly to the phosphorus biniodide by the use of proper atomic proportions of the constituents. The iodide forms dark red deliquescent six-sided plates, melting at 130° F. (55° C.), and the bromide yellow crystals melting to a red liquid.

[Note the importance in these reactions of using atomic proportions. See also the preparation of amorphous phosphorus by the action of iodine on yellow phosphorus.]

Phosphoric Fluoride (PF_5) is formed by the action of arsenious fluoride on phosphoric chloride ($5AsF_3 + 3PCl_5 = 5AsCl_3 + 3PF_5$.) It is a colorless non-inflammable gas, decomposed by water ($PF_5 + 4H_2O = H_3PO_4 + 5HF$), but not decomposed by electric sparks. It combines with ammonia ($5NH_3,2PF_5$).

Other compounds of oxygen and the haloids with phosphorus have been described, viz., *pyrophosphoryl chloride* ($P_2O_3Cl_4$), *phosphorous bromochloride* (PCl_3Br_2), *phosphoryl chlorobromide* ($POCl_2Br$), *phosphorous sulphobromochloride* ($PSCl_2Br$), etc.

Phospham (PN_2H).

Preparation.—By saturating phosphoric chloride (cooled by a freezing mixture) with ammonia gas, a white saline mass is obtained. This is now heated in a current of CO_2, until all the sal-ammoniac is sublimed. The residue constitutes *Phospham* ($PCl_5+7NH_3=5NH_4Cl+PN_2H$). (Gerhardt.)

Properties.—A yellowish-white, bulky, amorphous powder, termed phosphide of nitrogen by Rose. Rose overlooked the presence of hydrogen, phospham being unaffected by chlorine, and, provided no air be present, undergoing no change on being heated to redness.

ACTION OF AMMONIA ON PHOSPHORUS COMPOUNDS.

Phospham-imide [$PO(NH)(NH_2)$] is formed as a compound insoluble in water, by the action of ammonia on phosphoric chloride ($PCl_5+7NH_3+H_2O=PO(NH)(NH_2)+5NH_4Cl$).

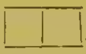
Phosphoric-oxy-Triamide [$PO(NH_2)_3$] is formed by the action of ammonia on the oxychloride ($POCl_3+6NH_3=PO(NH_2)_3+3NH_4Cl$) the body PON (phosphoryl nitride) remaining after ignition. The compounds $P_2O_3(NH_2)_3HO$ (pyrophosphotriamic acid) and $P_2O_3(NH_2)_2(HO)_2$ and $P_2O_3(NH_2)(HO)_3$ are also known, besides other bodies, such as $PO(NH_2)_3$ (phosphoryl triamide) and $PO(NH)(NH_2)$ (phosphamide).

CHAPTER VIII.

SULPHUR—SELENIUM—TELLURIUM.

SULPHUR.—Compounds of Sulphur with Oxygen and Hydrogen—Sulphurous anhydride and acid—Sulphuric anhydride and acid—Persulphuric Anhydride—Thiosulphuric acid—Dithionous and Dithionic acids—Trithionic acid—Tetrathionic acid—Pentathionic acid—Compounds of Sulphur and Chlorine—Compounds of Sulphur, Oxygen and the Haloids—Compounds of Sulphur and Phosphorus. SELENIUM.—Compounds of Selenium and Oxygen. TELLURIUM.—Compounds of Tellurium and Oxygen.

SULPHUR (S).

Atomic weight, 32 [*more accurately* 31·98]. *Molecular weight,* 64. *Molecular volume at* 1000° C. , *but at its boiling point only one-third of this. Atomicity, Hexad* (SO_3), *Tetrad* (SO_2), *Dyad* (H_2S). *Specific gravity of solids, various ; of vapor, at* 900° F. (482·2° C.), 6·617, *and at* 1904° F. (1040° C.), 2·23; *melts at* 239° F. (115° C.); *boils at* 836° F. (446° C.).

Synonyms.—*Pyrites* (*πυρ* fire); *Brimstone* (*Brennstein,* burning stone); *Sulphur* (*sal* salt, and *πυρ* fire).

History.—Sulphur was known in early times. It is mentioned by Moses, Homer, and Pliny, and is referred to by Geber as one of the principles of nature. It was considered by the alchemists to constitute the impurity of the baser metals. In the Middle Ages it was regarded as the principle of fire, and every combustible body was supposed to contain it.

Natural History.—(*a.*) In the *mineral* kingdom sulphur is found (1) in a *free* state in many volcanic districts, either in yellow crystals or in opaque amorphous masses embedded in blue clay and in fissures in gypsum and celestine (virgin or native sulphur). [When sulphuretted hydrogen, steam, and air are passed over calcic carbonate at 212° F. (100° C.) gypsum is formed, and sulphur deposited.] (2.) It is found in combination with hydrogen as H_2S in certain mineral waters (Harrogate), and as SO_2 in volcanic exhalations. It occurs combined with the metals, as *sulphides* (FeS_2, *iron pyrites ;* $Cu_2S.Fe_2S_3$, *copper pyrites;* PbS, *galena ;* ZnS, *blende ;* Sb_2S_3, *crude antimony ;* HgS, *cinnabar*). (3.) It is also found as *sulphates,* as *e.g.*, sulphates of *lime* (gypsum, $CaSO_4$) ; *baryta* (heavy spa, $BaSO_4$) ; *strontia* (celestine

$SrSO_4$); *magnesia* (Epsom salts, $MgSO_4$), and *soda* (Glauber salts, Na_2SO_4).

(β.) In the *vegetable* kingdom it is present in albumen, gluten, etc., and also in the acrid volatile oils, such as essence of mustard (C_4H_5NS); whilst (γ,) in the *animal kingdom* it is found as a constituent of albumen, fibrin, and casein, also in muscular tissue, hair, bile, etc.

Preparation.—(1.) By simply melting out the sulphur from its impurities. A loss of about 50 per cent. results.

(2.) By distilling the sulphur in earthenware retorts, and allowing the distillate to flow into water. This "rough sulphur," as it is called, is redistilled in iron retorts, and the sulphur collected either in cooled brickwork chambers (*flowers of sulphur*), or as a liquid which is afterwards cast into rolls (*roll sulphur*).

(3.) (*a.*) *By the distillation of iron or copper pyrites.*—The pyrites is heated either in close cylinders when one-third of the sulphur present is recovered ($3FeS_2=Fe_3S_4+S_2$), or in kilns by which one-half of the sulphur is collected ($3FeS_2+5O_2=Fe_3O_4+3SO_2+3S$). More than one-half may be obtained if the products be passed over heated carbon. (β.) *By distillation in the open air.* This is done in the case of copper pyrites as a preliminary stage to copper roasting. The pyrites, heaped on brushwood and fired from a central flue, is kept burning for months, and the sulphur therefrom collected in pits. The sulphur prepared from pyrites generally contains a little arsenic.

(4.) By distilling the spent oxide of iron used in gas purification. The oxide ($(Fe_2O_3,3H_2O)+3H_2S=2FeS+6H_2OH_2O+S$) by successive revivifications,* becomes charged with from 40 to 60 per cent. of sulphur ($2FeS+H_2O$(spent oxide)$+O_3=Fe_2O_3+H_2O+S_2$).

(5.) Sulphur is also prepared from the tank waste of alkali works:—in other words, from the residue of the black ash (a mixture of calcic sulphide and oxide) after the extraction of the sodic carbonate. Through this waste, air is blown, a thiosulphate and a persulphide being formed. The sulphur is thrown down from the solution with hydrochloric acid. (*See* SODIC CARBONATE.)

Varieties.—(1.) *Native Sulphur.*—This variety occurs naturally, formed, no doubt, by the action of H_2S on SO_2 in the presence of moisture ($5SO_2+5H_2S=H_2S_5O_6$ (pentathionic acid) $+4H_2O+5S$). It may also be obtained by the spontaneous evaporation of a solution of sulphur in carbon disulphide. It consists of transparent yellow crystals (octahedra), which are unaltered by exposure to air. It has a specific gravity of 2·05. It fuses at 239° F. (115° C.) It is the most stable of the sulphur allotropes, and is the ultimate condition assumed by all the other varieties.

(2.) *Yellow Sulphur.*—This variety may be crystallised by fusion

---

* By revivification the moist ferrous sulphide is changed into ferric hydrate and sulphur.

(oblique prisms). It is brownish yellow when first prepared, but is changed by exposure to air to an opaque yellow. This alteration is attended with a change of form (octahedra) and the evolution of heat. It has a specific gravity of 1·98. It fuses at 248° F. (120° C.).

(3.) *Ductile or Plastic Sulphur.*—This is prepared by pouring melted sulphur into cold water. By exposure to air it changes into the crystalline variety, becoming yellow and brittle, evolving heat during the alteration. A similar change may be effected by heating the ductile sulphur to 230° F. (110° C.).

(4.) *A Buff Amorphous Variety.*—This constitutes the insoluble residue that remains after exhausting the flowers of sulphur, or the ductile variety after prolonged exposure to air, with carbon disulphide.

(5.) *White Variety* (milk of sulphur).—This amorphous variety is prepared by precipitating a solution of sulphur in an alkali (an alkaline polysulphide) with an acid ($K_2S_5+2HCl=2KCl+H_2S+2S_2$). It is soluble in bisulphide of carbon.

A Black Variety has also been described by Magnus, as well as one of a *red* color, but of these our knowledge is not complete.

These allotropic forms of sulphur may be thus tabulated :—

	1. Octahedral. Native or Crystallized from CS_2.	2. Prismatic. Yellow Sulphur.	3. Ductile or Plastic Sulphur.	4. Amorphous Sulphur.	5. White Amorphous Sulphur.
Color	Transparent yellow.	Brownish yellow.	Deep amber.	Buff.	White.
Form	Crystals—Octahedra with rhombic base.	Oblique prisms.	Plastic amorphous mass.	Amorphous powder.	Amorphous powder.
Specific grav.	2·05.	1·98	1·95.	1·95.	
Melting point	239° F. (115° C.)	248° F. (120° C.)			
Action of CS_2	Soluble.	Soluble (changed into form No. 1).	Insoluble.	Insoluble.	Soluble.

Properties.—The properties of sulphur differ according to the variety.

(*α.*) *Sensible and Physiological.*—Sulphur is met with in commerce, either as roll sulphur or as flowers of sulphur. It crystallizes in two distinct forms (dimorphous), viz., in octahedra and in oblique prisms. Ordinary sulphur is yellow, but the colors of its allotropes are various. Native sulphur is transparent, but all the other forms are opaque. It has neither taste nor smell. Its medicinal action is mildly laxative.

(*β.*) *Physical.—The specific gravity* of the *transparent crystalline* variety is 2·05; of the *prismatic* 1·98; of the *ductile* and the *amorphous powder* 1·95. The specific gravity of the vapor at 900° F. (482·2° C.) is 6·617, whilst at 1904° F. (1040° C.) it is 2·222. (Deville.) Thus, at 1904° F. sulphur vapor becomes dilated to three times the bulk it occupies at 900° F. This fact is important. We mean by specific gravity the weight of a body compared with an equal volume of dry air at the same temperature and pressure. Hence the actual temperature, in the case of most gases and vapors, is of no consequence. For example, whether oxygen be compared with air at 60° F., or with air at 600° F., so long as both oxygen and air be at the same temperature when the comparison is made, their weights relatively would be as 1·1057 to 1·000. In the case of sulphur vapor, however, its specific gravity at 900° F. is 6·617; that is, it is six and a-half times heavier than air at 900° F., the atom being, therefore, 96 times as heavy as hydrogen. It follows from this that, the atomic weight of sulphur being 32, the atom would only occupy $\frac{1}{3}$ of a volume. But at 1904° F. its specific gravity becomes 2·222 ; that is, the sulphur vapor is about two and a-quarter times as heavy as air at 1904° F. It is evident, therefore, that sulphur vapor is only a true gas at this higher temperature, one atom of sulphur occupying one volume, and being 32 times the weight of a hydrogen atom.

Action of Heat.—Sulphur is a bad conductor of heat. When held in the hand it crackles, owing to unequal expansion. It is slightly volatile at ordinary temperatures, and freely volatile at 280° F. (137·8° C.). The octahedral variety fires at 239° F. (115° C.), and the prismatic at 248° F. (120° C.). A slight phosphorescence occurs when sulphur is heated to a lower temperature than the point of ignition. It boils at 836° F. (446·6° C.).

The action of heat on sulphur is remarkable, and may be examined under the three heads of (1) Fluidity, (2) Color, and (3) Form :—

(1.) *In respect of Fluidity.*—At a temperature of from 250° to 280° F. (121° to 138° C.) sulphur becomes liquid ; at 350° F. (170° C.) it becomes thick and viscid; and at 500° F. (260° C.) it again becomes liquid.

(2.) *In respect of Color.*—The sulphur remains yellow to 280° F. (137·8° C.). At from 280° F. to 350° F. (138° to 177° C.) it becomes orange ; at from 350° to 400° F. (177° to 204° C.) it turns of a reddish color ; at from 400° to 500° F. (204° to 260° C.) it becomes dark brown ; whilst at 600° F. (316° C.) it becomes black.

(3.) *In respect of Form.*—When sulphur is heated to 239° F.(115° C.) and slowly cooled, its crystals are right prisms; when heated above this temperature and cooled slowly, it forms oblique prisms; whilst, if heated above 500° F. (260° C.), and then cooled rapidly, it assumes the elastic and amorphous modification.

We may state these facts generally as follows :—When the sulphur is heated to 280° F. (138° C.) it becomes liquid. As the heat is continued, it gradually becomes thick and viscid, until at 350° F. (176·7° C.) the sulphur has become so thick that it cannot be poured out of the vessel when inverted. It remains at this temperature for some time, notwithstanding the continuous application of heat. At from 350° to 500° F. its fluidity is restored, and it assumes a dull brown color. If it be now poured into cold water, the elastic variety is produced. In the change from the elastic to the common yellow modification, the heat absorbed at 350° F. (176·7° C.) is evolved. When the melted sulphur is allowed to cool, it passes through the same stages *inversely* as when heated, that is, it first becomes viscous, then fluid, and finally solid.

Sulphur is a non-conductor of electricity, becoming negatively electrical by friction. All the varieties of sulphur are insoluble in water, but are soluble in alcohol, chloroform, and ether, and (excepting the amorphous modification) in turpentine, chloride of sulphur, benzene, the fixed oils, and more particularly in carbon disulphide.

(γ.) *Chemical.*—Sulphur is combustible at from 450° to 500° F. (235° to 260° C.), burning with a blue flame, and forming SO_2. Air in the presence of moisture effects some oxidation of finely divided sulphur, even at common temperatures. It combines freely with all the non-metals except nitrogen, and with all the metals (to form sulphides), many of which burn in its vapor. In its chemical relations it is closely allied to oxygen, forming compounds analogous to basic and acid oxides.

Chemically, according to Berthelot, sulphur may be divided under two heads :—

(1.) Where it is *electro-negative*, that is, where it is separated from a compound at the positive pole of the battery, as in H_2S. This form, which includes octahedral and prismatic sulphur, is *soluble* in carbon disulphide.

(2.) Where it is *electro-positive*, that is, where it is separated at the negative pole of the battery, as in SO_2 or in S_2Cl_2. This form, which includes plastic and amorphous sulphur, is *insoluble* in carbon disulphide.

Concentrated *nitric and sulphuric acids* act on sulphur slowly, the former converting it into sulphuric acid, and the latter into sulphurous acid. It is changed into sulphuric acid by the action of nitric acid and potassic chlorate. The alkalies dissolve phosphorus when heated with it, a mixture of a hyposulphite and a sulphide of the metal being formed.

Uses.—In the *arts*, sulphur is used in match-making, in the preparation of vulcanised caoutchouc, in bleaching, and in the manufacture of gunpowder and oil of vitriol. In *medicine* it is used as a laxative, and in various forms of cutaneous diseases. In the preparation of the *sulphur precipitatum* (milk of sulphur), the pharmacopœia directs five parts of sulphur to be boiled in water with three parts of lime. Thus, a calcium hyposulphite and polysulphide are formed ($3CaH_2O_2 + 6S_2 = 2CaS_5 + CaS_2O_3 + 3H_2O$). The sulphur in the solution is now precipitated with hydrochloric acid ($2CaS_5 + CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + 6S_2$). The sulphurous acid set free by the action of the acid on the hyposulphite decomposes the sulphuretted hydrogen set free by the action of the acid on the sulphide ($4H_2S + 2SO_2 = 3S_2 + 4H_2O$). "Milk of sulphur," however, is often precipitated by adding sulphuric acid instead of hydrochloric acid, in this way becoming largely adulterated with calcic sulphate ($2CaS_5 + CaS_2O_3 + 3H_2SO_4 = 3CaSO_4 + 3H_2O + 6S_2$). This adulteration may be known by a residue of calcic sulphate being left on ignition.

Sometimes a trace of arsenic is present in the *sulphur sublimatum* B.P. (flowers of sulphur) prepared from pyrites.

COMPOUNDS OF SULPHUR WITH OXYGEN (SULPHUR ACIDS).

Sulphur Oxide or Anhydride.	Formula.	+Water.	=Sulphur Acid.	Name of acid.
Sulphurous ..	SO_2	$+H_2O$	$=H_2SO_3$	Sulphurous acid.
Sulphuric ..	SO_3	$+H_2O$	$=H_2SO_4$	Sulphuric acid.
Persulphuric ..	S_2O_7			
			Polythionic Acids (θειον sulphur.) $H_2S_2O_3$	Thiosulphuric acid.
			$H_2S_2O_4$	Dithionous acid.
			$H_2S_2O_6$	Dithionic acid.
			$H_2S_3O_6$	Trithionic acid.
			$H_2S_4O_6$	Tetrathionic acid.
			$H_2S_5O_6$	Pentathionic acid.

Sulphurous Anhydride, SO_2.

Molecular weight, 64. *Molecular volume*, ☐☐. *Relative weight*, 32. *Specific gravity of gas* (0·0693 × 32) 2·217; *of liquid*, 1·38. 1 *litre of the gas weighs* (0·0896 × 32) 2·867 *grms., and* 100 *cubic inches* 68·576 *grains.*

Synonyms.—*Sulphur Dioxide; Volatile Spirits of Sulphur; Phlogisticated Vitriolic Acid.*

History.—The irritation produced by burning sulphur is mentioned by Homer and Pliny. It is said to have caused the death of the elder Pliny (A.D. 79), in his curious enquiry into the eruption of Vesuvius. Its properties were studied by Stahl and by Priestley (1774), the latter of whom determined its real nature by burning sulphur in pure oxygen.

Natural History.—It is found in the air of volcanic districts and in that of towns, in the former case issuing from volcanoes, and in the latter evolved from burning coal, or from trade operations, such as roasting copper pyrites and other sulphur ores.

Preparation. — (1.) By burning sulphur in air or oxygen ($S+O_2=SO_2$).

(2.) By heating sulphuric acid with copper, mercury, or other metal not evolving hydrogen with sulphuric acid, [otherwise the SO_2 would be mixed with hydrogen]:—

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

Copper + Sulphuric acid = Cupric sulphate + Sulphurous anhydride + Water.

(3.) By heating sulphuric acid with carbon or other organic body, in which case CO_2 is also evolved:—

$$2H_2SO_4 + C = 2SO_2 + CO_2 + 2H_2O.$$

Sulphuric acid + Carbon = Sulphurous anhydride + Carbonic anhydride + Water.

(4.) By heating together sulphur and manganese dioxide:—

$$S_2 + MnO_2 = SO_2 + MnS.$$

Sulphur + Manganese dioxide = Sulphurous anhydride + Manganous sulphide.

(5.) By heating together (*a*) sulphur and dehydrated ferrous sulphate, or (*β*) sulphuric acid and sulphur [*a*, ($FeSO_4+S_2=FeS+2SO_2$); *β*, ($2H_2SO_4+S=3SO_2+2H_2O$)].

The gas must be collected in dry bottles by displacement or over mercury.

Properties. (*a*.) *Sensible.* — A colorless gas, having a strong brimstone odor.

(*β*.) *Physiological.*—It rapidly destroys life when in a concentrated form. When very dilute the irritation produced in the first instance rapidly passes off, the animal becoming tolerant of a somewhat large quantity. One part in 10,000 parts of air is destructive to plant-life.

Proportion of SO_2 in 10,000 of air.	Physiological effects and chemical reactions.
4·34	Air irrespirable. Acts instantly on iodic acid and starch.
2·00	Air strong both to taste and smell. Acts on starch and iodic acid in 30 seconds.
0·86	Air strong to smell and irritating. Acts on test paper in 2 minutes.
0·1	Smell perceptible. Acts on test paper after some time.

(*γ*.) *Physical.*—The gas has a specific gravity of 2·217; 100 cubic inches weigh 68·576 grains. It is freely soluble in water and in alcohol. By a pressure of three atmospheres at common temperatures, or by a cold of 44·6° F. (7° C.) at two atmosphères, it is condensed into a transparent liquid having a specific gravity of 1·38. Liquefaction may also be effected spontaneously by mixing one part of sulphur and five parts of sulphuric anhydride ($2SO_3+S=3SO_2$) in a strong glass tube. The liquid solidifies at —105° F. (—76° C.). The solid thus formed is colorless and transparent. At a temperature of 2192° F. (1200° C.) or by the action of a beam of sunlight (Tyndall) sulphurous anhydride decomposes, SO_3 being formed from a part of the undecomposed SO_2 uniting with the oxygen ($3SO_2=2SO_3+S$).

Liquid sulphurous anhydride dissolves bitumen, phosphorus, sulphur, iodine, etc.

Solubility in water.—*See* Sulphurous Acid.

(δ.) *Chemical.*—The composition of SO_2 may be determined synthetically. Inflame a piece of sulphur (by electricity) in a known bulk of oxygen standing over mercury. Combustion being complete, the volume of SO_2 formed will be found to be identical with that of the oxygen employed.

Sulphurous anhydride first reddens and afterwards bleaches litmus. It will not support the combustion of a taper. Most fire extinguishers contain sulphur together with resin and nitre.

It is a powerful *reducing agent,* owing to its tendency to become oxidised. When a sulphurous acid solution is heated in a sealed tube to 340° F. (171° C.) it yields free sulphur and sulphuric acid, one portion of the sulphurous anhydride becoming oxidised at the expense of another portion ($3SO_2+2H_2O=2H_2SO_4+S$). It reduces nitric acid ($2HNO_3+SO_2=H_2SO_4+N_2O_4$), iodic acid (setting free iodine), and also chromic, arsenic, and permanganic acids.

It is a powerful bleaching agent. It does not, however, destroy the coloring matter (as in the case of chlorine, the bleaching action of which is due to oxidation), but merely forms colorless compounds with the coloring matters. The color of the article bleached with SO_2, may be restored by the action of an alkali or of a stronger acid.

Action on Chlorine.—Sulphurous anhydride combines with chlorine in equal volumes under the influence of bright sunshine, to form *chlorosulphuric acid* or *chloride of sulphuryl* (SO_2Cl_2), a colorless liquid emitting very acrid irritating vapors. This body does not combine with bases. It is decomposed by water, forming *sulphuric* and hydrochloric acids.

NOTE.—*The chloride of thionyl* ($SOCl_2$) formed by the action of hypochlorous acid gas on a solution of sulphur in subchloride of sulphur, is also decomposed by water, *sulphurous* and hydrochloric acids being formed. With iodine in the presence of moisture (the SO_2 not exceeding 0·05 per cent.) hydriodic acid is formed (SO_2+

$2H_2O+I_2=2HI+H_2SO_4$). The H_2SO_4+HI, however, effect mutual decomposition ($H_2SO_4+2HI=SO_2+I_2+2H_2O$).

Action on the Metals.—Sodium and potassium burn in sulphurous anhydride, forming a mixed oxide and sulphide. A similar result occurs when iron, lead, tin, or zinc are heated in the gas ($SO_2+3Zn=ZnS+2ZnO$).

When sulphurous anhydride or the acid is passed into or mixed with a solution of a *metallic hydrate,* a sulphite is formed. It is to be noted that—

(*a*.) If the acid be in excess, *an acid sulphite* ($MHSO_3$) is formed ($KHO+SO_2=KHSO_3$), but that—

(*β*.) If the hydrate be in excess, *a normal or neutral sulphite* (M_2SO_3) is formed ($2KHO+SO_2=K_2SO_3+H_2O$).

Brought into contact with *metallic peroxides,* sulphurous anhydride forms sulphates ($PbO_2+SO_2=PbSO_4$).

In the presence of moisture, sulphurous acid decomposes sulphuretted hydrogen, pentathionic acid being formed ($10SO_2+10H_2S=5S_2+8H_2O+2H_2S_5O_6$). The sulphur thrown down during this reaction is electro-positive, and insoluble in carbon disulphide.

Uses.—Sulphurous anhydride is a powerful antiseptic and disinfectant. Liquid sulphurous acid, evaporated rapidly in vacuo, produces a cold of —104·8° F. (—76° C.).

Sulphurous Acid (H_2SO_3).

Water dissolves 80 times its volume of sulphurous anhydride at 32° F. (0° C.) forming a sulphurous anhydride solution (Sulphurous Acid). As a fact, no definite hydrate is known. The solution of the gas, however, when cooled below —40° F. (—40° C.), yields a crystalline hydrate (H_2SO_3, $8H_2O$), which fuses at 39·2° F. (4° C.). Sulphurous acid expels carbonic anhydride from its compounds. It is readily decomposed by heat into sulphurous anhydride and water, and freely absorbs oxygen from the air, forming sulphuric acid. In the presence of nascent hydrogen it forms sulphuretted hydrogen. It dissolves and is decomposed by those metals which evolve hydrogen with hydrochloric acid. It is a dibasic acid, forming two classes of salts, viz., acid and normal sulphites.

Tests.—(1.) Its brimstone odor.

(2.) *Starch and iodic acid.* The SO_2 reduces the iodic acid, the free iodine turning the starch blue.

Uses.—In *the arts* it is employed as a bleaching agent for straw, wool and hair, nuts, etc., and also as an '*antichlor*' to get rid of the excess of chlorine in goods bleached by that gas ($SO_2+2H_2O+Cl_2=H_2SO_4+2HCl$). It is also used as an antiseptic, to prevent fermentation, for 'curing' vegetable and fruit extracts, and as a meat preservative. Thus beer and wine casks are first sulphured. Its chief use is in the oil of vitriol manufacture. It is largely employed as a disinfectant.

Sulphuric Anhydride, SO_3.

Molecular weight, 80. *Molecular volume*, ☐☐. *Specific gravity*, 1·95. *Melts at* 60·8° F. (16° C.). *Boils at* 114·8° F. (46° C.).

Synonyms.—*Sulphur trioxide ; Sulphuric oxide ; Anhydrous sulphuric acid.*

Preparation.—(1.) By passing sulphurous anhydride (2 vols.) and oxygen (1 vol.) either over heated spongy platinum, or through a tube heated to redness containing oxide of copper and sesquioxide of chromium. The SO_3 is to be condensed in a cooled receiver (Wöhler) ($SO_2+O=SO_3$) :—

(2.) By heating a mixture of sulphuric acid and phosphoric anhydride :—

H_2SO_4 + P_2O_5 = SO_3 + $2PHO_3$.
Sulphuric acid + Phosphoric anhydride = Sulphuric anhydride + Metaphosphoric acid.

(3.) By distilling Nordhausen sulphuric acid, and collecting the products in an ice-cold receiver [$(H_2SO_4, SO_3)=H_2SO_4+SO_3$].

(4.) By the action of heat on anhydrous sodic bisulphate, prepared by heating hydric sodic sulphate to redness ($2NaHSO_4=Na_2O,2SO_3+H_2O$).

$Na_2O,2SO_3$ = Na_2SO_4 + SO_3.
Sodic bisulphate = Sodic sulphate + Sulphuric anhydride.

Properties. (*a.*) *Sensible and Physical.*—A white, odorless, asbestos-like body, capable of being moulded with the fingers. It has a specific gravity of 1·95. It melts at 60·8° F. (16° C.), and boils at 114·8° F. (46° C.)

Two modifications of the anhydride are recorded :—α anhydride is formed by *rapidly* cooling the melted anhydride, when it solidifies at 60·8° F. (16° C.) in prisms, and β anhydride by keeping the liquid for some time at 77° F. (25° C.), when it solidifies in needles which melt at or about 122° F. (50° C.).

It liquefies by exposure to air, and is decomposed by heat into oxygen and sulphurous anhydride.

(β.) *Chemical.*—It is not acid to dry litmus. It does not burn the dry skin. It dissolves sulphur, forming with it definite compounds. It has a great affinity for moisture, fuming in the air, and hissing when dropped into water, instantly forming sulphuric acid, which cannot, after combination, be separated into water and the anhydride. With ammonia gas it forms ammonic sulphamate.

SULPHURIC ACID, $H_2SO_4=98$.

Synonyms.—*Vitriolic acid; Oil of Vitriol; Oil of Sulphur; Vitriol; Spirit, or Essence of Vitriol; Dihydric Sulphate; Protohydrate of Sulphuric acid.*

History.—Probably known to Geber in the 8th century. It is mentioned by Basil Valentine (15th century), and was fully and accurately described by Dornœus in 1570.

Natural History.—(α.) In the *mineral* kingdom it is found in a free state in the "vinegar springs" of volcanic districts, and largely in combination with lime, etc. (β.) In the *vegetable* kingdom it is found combined with alkalies in the juices of plants; and (γ.) in the *animal* kingdom it is found to a small extent free, as in the salivary secretions of certain animals (Dolium Galea, 2·7 per cent.), and to a large extent in combination.

Preparation.—(1.) Either by the oxidation of sulphur by boiling it in aqua regia, or by its exposure to air in the presence of water ($S_2+3O_2+2H_2O=2H_2SO_4$); also by the oxidation of sulphurous acid, either by exposure to air, to oxygen, or to peroxide of hydrogen ($H_2SO_3+O=H_2SO_4$).

(2.) By the action of water on sulphuric anhydride ($SO_3+H_2O=H_2SO_4$).

(3.) By the distillation of dry ferrous sulphate (green vitriol), prepared by the oxidation of iron pyrites. This is the old plan, but is still adopted at Nordhausen, in Saxony. (Basil Valentine.) The acid produced by this process has the formula H_2SO_4,SO_3. Colcothar (Fe_2O_3) is left in the retort after the distillation is complete.

(4.) By passing *sulphurous anhydride* (SO_2), vapors of *nitric acid* (HNO_3), *steam* (H_2O), and *air* into a leaden chamber, so arranged as to secure their perfect admixture. The passage of the gases is effected by a tall chimney connected with the Gay Lussac scrubber. A shallow layer of water covers the bottom of the chamber. (Roebuck, 1720.)

(α.) The *sulphurous anhydride* is generated by burning either *crude sulphur*, or by roasting *pyrites* (which may contain 30 to 35 per cent. of sulphur), or by heating the *spent oxide of gas works* (which often contains 40 to 60 per cent. of sulphur). About 95 per cent. of the sulphur thus employed is converted into sulphuric acid.

(β.) The *nitric acid* is generated by the action of sulphuric acid on sodic nitrate. For every 100 parts of sulphur about 2 parts of sodic nitrate are required.

(γ.) The steam is derived from a special water boiler. Sprengel has suggested the use of a fine water spray whereby a certain saving of fuel is effected.

(δ.) The *air* is provided in due quantity by maintaining a constant current through the leaden chamber.

Roughly the changes that occur may be stated as follows :—The nitric acid in the presence of moisture oxidizes the sulphurous anhydride, thereby converting it into sulphuric acid. The nitric acid (HNO_3) becomes, by constantly parting with its oxygen, nitric oxide (N_2O_2). This nitric oxide immediately takes oxygen from the air, and becomes nitric peroxide (N_2O_4), which is again capable of converting fresh sulphurous anhydride into sulphuric acid. Thus, theoretically, a small quantity of nitric acid vapor in the presence of air, should convert an indefinite quantity of sulphurous anhydride into sulphuric acid, the N_2O_2 merely acting as the carrier of oxygen from the air to the SO_2.

The following are the more accurate details of the reaction :—

(α.) The sulphurous acid is first oxidized by the nitric acid, nitric peroxide being set free :—

$$SO_2 + 2HNO_3 = H_2SO_4 + N_2O_4.$$

(β.) In the presence of steam the N_2O_4 becomes nitric acid (HNO_3) and nitric oxide (N_2O_2) :—

$$3N_2O_4 + 2H_2O = 4HNO_3 + N_2O_2.$$

(γ.) The HNO_3 thus formed, instantly oxidizes more sulphurous anhydride, and the N_2O_2 takes oxygen from the air, becoming N_2O_3 and N_2O_4, which also oxidizes the SO_2, N_2O_2 being re-formed :—

$$N_2O_3 + SO_2 + H_2O = H_2SO_4 + N_2O_2.$$

This N_2O_2 again becomes N_2O_3 and N_2O_4, etc.

If *little or no steam be present* in the chamber, a white flaky crystalline body ($N_2O_3,2SO_3$?) is formed, produced by the direct combination of nitrous anhydride or nitric peroxide with oxygen and sulphurous anhydride. When this falls into the water at the bottom of the chamber, it is decomposed, sulphuric acid being produced, and nitric oxide set free. This latter coming into contact with the air, immediately becomes N_2O_4, and again forms fresh flakes of this white crystalline body by combining with sulphurous anhydride. But when *steam is present*, this white body is not formed, but the sulphuric acid is at once produced, and falls as a fine spray into the water.

Properly, nothing should escape from the leaden chamber, except atmospheric nitrogen. Such theoretical accuracy is not, however, of practical attainment. To guard against loss and nuisance, the outlet of the leaden chamber is usually provided with two coke scrubbers. The first of these (the Gay Lussac tower) is kept moist with concentrated sulphuric acid to retain the oxides of nitrogen, whereby a nitrous sulphuric acid (or sulphuric acid with peroxide of nitrogen in solution) is formed, and from which the nitrogen oxide is recovered. [To effect this the nitrous sulphuric acid is allowed to trickle over flints placed in a scrubber at the inlet, called a Glover's Tower, a weak chamber acid at the same time being allowed to mix with it.

The nitric peroxide being insoluble in a dilute acid, is therefore liberated by the admixture, and is carried by the hot and free SO_2 (which is also passed through the tower) into the leaden chamber. The hot sulphurous acid also generates steam by contact with the dilute acid]. In the second scrubber at the outlet the coke is moistened with water, the liquor from which is allowed to flow on to the floor of the leaden chamber.

When the acid in the chamber reaches a gravity of from 1·45 to 1·6, it is drawn off, since, if it were allowed to become of greater concentration, it would dissolve nitric oxide. This forms *chamber acid*, and is used in the salt cake manufacture. The chamber acid is concentrated first of all by evaporation in leaden pans until it has a gravity of 1·72, beyond which the acid would seriously affect the lead. This forms *the brown acid* of commerce, and is used in the manufacture of superphosphate, and for other rough purposes. It is afterwards distilled in glass or platinum vessels (the weak distillate being used for the leaden chamber) until the acid in the retort has a gravity of 1·842. This forms the English oil of vitriol, or O.V.

Varieties.—The anhydride forms four definite compounds with water.

(1.) *Nordhausen sulphuric acid*, or *fuming oil of vitriol* (H_2SO_4,SO_3).

Synonyms: Pyrosulphuric acid; Dehydric disulphate.

Preparation. (i.) By the distillation of dried ferrous sulphate ($FeSO_4,H_2O$), a hexabasic ferric sulphate (Fe_2SO_6) being first formed, which by heat breaks up into Fe_2O_3 and SO_3.

(ii.) By the solution of sulphuric anhydride in concentrated sulphuric acid.

Properties. A fuming acid. Specific gravity, 1·9. It is used for dissolving indigo. By a moderate heat it is decomposed into H_2SO_4 and SO_3.

(2.) *Oil of vitriol*, or *true sulphuric acid* (H_2SO_4). This cannot be prepared by merely boiling down a weak acid, the acid thus obtained always having a composition of $H_2SO_4,\frac{1}{12}H_2O$, or $12SO_3,13H_2O$. By exposing this strong acid, however, to a freezing mixture, the acid, having the formula H_2SO_4, crystallizes out. The crystals melt at 51° F. (10·5° C.), and boil at 640° F. (470° C.), when the liquid gives off sulphuric anhydride, the resulting acid solution having the formula $12SO_3,13H_2O$.

(3.) *Glacial sulphuric acid* (H_2SO_4,H_2O). This is prepared by cooling an acid of specific gravity 1·78 to 47° F. (8·3° C.), when rhombic crystals of H_2SO_4,H_2O separate. It boils at 400° F. (205° C.), giving off a weaker acid.

(4.) *Graham's acid* ($H_2SO_4,2H_2O$). This is prepared by evaporating a dilute acid 'in vacuo' at 212° F. (100° C.), until it ceases to lose weight. Specific gravity, 1·62. It boils at 379° F. (193° C.).

These facts are tabulated by Miller as follows :—

	Formula.	Fusing point.		Boiling point.		Specific Gravity.
		°C.	°F.	°C.	°F.	
Sulphuric anhydride	SO_3	18·3	65	35	95	1·95
Nordhausen sulphuric acid	H_2SO_4,SO_3	35·0	95	52·2	126	1·9
True sulphuric acid, Oil of vitriol	H_2SO_4	10·5	51	338	640	1·848
Glacial acid	H_2SO_4,H_2O	8·3	47	205	400	1·780
Graham's acid	$H_2SO_4,2H_2O$			193	379	1·620

Impurities, and Tests for the Impurities of Sulphuric Acid.

(1.) *Compounds of Oxygen and Nitrogen* (derived from the nitric acid used in the manufacture),

Tests.—(*a.*) Turns ferrous sulphate an olive green color. (*β.*) Bleaches dilute indigo.

(2.) *Sulphurous Acid* (derived from the unoxidised SO_2 in the leaden chamber).

Test.—Sulphuretted hydrogen is set free when zinc is added to the acid, impure from this cause.

(3.) *Arsenic* (derived from the pyrites).

Tests.—(*a.*) Marsh's test. (*β.*) Neutralise the acid with potassic carbonate, acidulate with hydrochloric acid, and pass sulphuretted hydrogen through the solution, when the arsenic will be precipitated as a yellow sulphide (orpiment).

(4.) *Lead* (derived from the leaden chamber).

Test.—Mix the acid with about 10 times its bulk of water, when the lead sulphate, which is insoluble in a weak acid, will be precipitated. Boil the precipitate in a solution of sodic carbonate ; filter ; test one-half of the filtrate with potassic iodide, and the other half with sulphuretted hydrogen.

(5.) *Saline impurities* (derived either from the nitre, or else purposely added to increase the gravity of the acid).

Test.—Evaporate to dryness for residue.

(6.) *Carbonaceous Matter* (derived from the accidental admixture of the acid with organic matter).

Test.—The color of the acid.

Purification of Sulphuric Acid.

Dilute 1 part of the acid with 5 parts of water. Pass sulphuretted hydrogen through the mixture for 5 or 6 hours. Allow the solid impurities to subside, and syphon off the clear liquor. Mix this with a teaspoonful of common salt, and distil, rejecting the first portion that passes over.

Properties.—(α.) *Sensible.*—An oily liquid, without color or smell when pure, but ordinarily more or less colored, from dissolved organic matter. It is an intensely corrosive poison. The Nordhausen acid differs from the other acids by fuming in the air, owing to the separation of a minute trace of sulphuric anhydride.

(β.) *Physical.*—The Nordhausen acid has a gravity of 1·9. Different acids have different gravities, depending on their respective strength. (*See* Table II. in Appendix.)

Action of Heat.—The *boiling point* of the acids varies. *English acid* boils at 640° F. (338° C.) ; the *brown acid,* at 435° F. (224° C.); and *chamber acid,* at 348° F. (175·5° C.). All the acids may be frozen by a cold somewhere about —29° F. (—34° C.), but they require a temperature considerably above this for their re-liquefaction.

The acid does not volatilise at the ordinary temperature of the air. Hence, when a dilute acid is dropped on cloth, it becomes concentrated from the gradual evaporation of the water. By warming the cloth before the fire, the acid on the fabric may be rendered sufficiently concentrated to char the cloth.

When the vapour of sulphuric acid is heated to 878° F. (470° C.) it is dissociated, that is, partially decomposed into SO_3 and H_2O, which products of dissociation reunite on condensation.

The specific gravity of the vapor just above the boiling point of the acid is 2·15, a number that represents 2 volumes of H_2O and 2 volumes of SO_3 condensed into 3 volumes ; but when the heat is increased to 878° F. (470° C.), these 3 volumes are found to occupy 4 volumes, (*i.e.* 2 vols. of $H_2O + 2$ vols. of SO_3 uncondensed), the vapor, at this higher temperature, having a gravity of 1·692. (*See* page 15.)

When the acid is dropped upon, or the vapor passed over red-hot platinum, steam, sulphurous anhydride and oxygen are formed. By solution in water, the steam and sulphurous acid may be absorbed, and the oxygen obtained in a pure state. (*See* page 72.)

(γ.) *Chemical.*—Sulphuric acid is very acid to litmus. The strong acid when cold, acts feebly on the metals, but when boiled in contact with them (excepting in the case of gold, platinum, iridium and rhodium) it undergoes decomposition, sulphurous anhydride being evolved, and a sulphate of the metal formed ($M'' + 2H_2SO_4 = M''SO_4 + SO_2 + 2H_2O$). When a weak acid is poured on the more oxidizable metals (such as zinc, iron, etc.) hydrogen is evolved, and a sulphate of the metal formed ($Zn + H_2SO_4 = H_2 + ZnSO_4$).

Sulphuric acid evolves oxygen when added to metallic peroxides, but with all oxides it forms sulphates. The concentrated acid is also decomposed when boiled with charcoal or sulphur, sulphurous anhydride being set free.

The affinity of the acid for water is very great. It was found (April, 1870) that 100 grains of acid (Sp. Gr. 1·842) freely exposed to the air in a basin, absorbed 120 grains of water during four days, its bulk being thereby increased threefold, and its density lowered to 1·340. The absorption of water, however, by larger quantities is not in like proportion :—1,000 grains of the same acid freely exposed to the air in a similar manner, only absorbed 232 grains of water in 24 hours, 430 grains in 48 hours, 580 grains in 72 hours, 690 grains in 96 hours, and 770 grains in 120 hours. The acid finally had a specific gravity of 1·310, this being the point of dilution at which both weak and strong solutions of the acid arrive when exposed to the air. This explains the use of the acid in the laboratory as a desiccating and dehydrating reagent. The charring of organic bodies, such as sugar, produced by the action of the acid, is due to this affinity for water.

A great rise of temperature and consequent condensation, occurs when sulphuric acid is mixed with water. The heat produced is a little greater when the water is poured into the acid, than when the acid is poured into the water.

Table showing the Heat and Condensation resulting from various Mixtures of Sulphuric Acid and Water. Temperature of Day, 22·22°C. (72° F.)

Sp. Gr. of the Acid used.	Weight of Acid used in Grains.	Bulk of Acid used.	Weight of Water used in Grains	Bulk of Water used.	Temperature produced.		Bulk of Resulting Fluid when cold.	Sp. Gr. of Resulting Fluid.
					°F.	°C.		
1·840	3000	℥ iij & ʒ vj	1000	℥ ij & ʒ ij	266	130·00	℥ v	1·616
1·840	2000	℥ iiss	do.	do.	252	122·20	℥ iv	1·548
1·840	1000	℥j & ʒ ij	do.	do.	210	98·88	℥ iij	1·390
1·840	500	ʒ v	do.	do.	198	92·22	℥ ij & ℥ ivss	1·245
1·840	250	ʒ iiss	do.	do.	130	54·44	ʒ ij & ʒ iij	1·136
1·616	1616	℥ ij & ʒ ij	do.	do.	119	48·33	do.	1·282
1·548	1548	do.	do.	do.	108	42·22	do.	1·246
1·390	1390	do.	do.	do.	95	35·00	do.	1·170
1·245	1245	do.	do.	do.	81	27·22	do.	1·074
1·138	1138	do.	do.	do.	78	25·55	do.	1·055

Certain *organic bodies*, such as starch and cellulose, are carbonized by the strong acid, whilst dilute acids convert them into grape sugar. The acid coagulates albumen, forming with it, as with other organic bodies, definite chemical compounds which are insoluble.

Sulphuric acid is a powerful dibasic acid, and displaces other acids, such as nitric, hydrochloric, etc., from their compounds. It forms two classes of sulphates, viz., an acid sulphate, where one hydrogen only is replaced by a metal ($M'HSO_4$), and a normal sulphate, where both hydrogens are replaced by a metal or metals (M'_2SO_4 or $M''SO_4$).

Tests.—(1.) *Taste.* The solution is perceptibly sour when it contains 1-1000th part of anhydrous acid.

(2.) *Action on Litmus.* The reddening of blue litmus is distinct when 1 part of anhydrous acid is diluted with 6,000 of water.

(3.) *Calcic Chloride* gives a copious white precipitate, insoluble in dilute nitric and hydrochloric acids. A turbidity is distinctly apparent when the solution contains only 0·014 per cent. of acid.

(4.) *Plumbic Acetate* gives a white precipitate, insoluble in dilute acids.

(5.) *Baric Chloride* (or baric nitrate) gives a white precipitate, insoluble in free acids and in caustic alkalies. The turbidity is apparent with a solution consisting of 1 part of acid in 62,500 of water.

The baryta salt must never be added to a *neutral* or to an *alkaline* solution, otherwise carbonic, phosphoric, oxalic acids, etc., may be precipitated, all of which are, however, soluble in nitric or hydrochloric acid. To prove that the precipitate is baric sulphate, it must be collected and dried, mixed with about four times its bulk of powdered wood charcoal, and heated to redness for some time in a platinum crucible. By this means the $BaSO_4$ will be reduced to BaS. Add to the cold residue a few drops of dilute hydrochloric acid, and apply heat, when sulphuretted hydrogen will be generated, which may be known by its blackening moistened lead paper.

(6.) *Nitrate of Strontia* gives a white precipitate, partially soluble in water and in dilute acids.

(7.) If sulphuric acid be gently heated in a test tube with some pieces of wood, copper, or mercury, etc., sulphurous anhydride is evolved, and may be known by its imparting a blue tint to a piece of starch paper moistened with iodic acid.

(8.) A trace of *veratria* added to a drop of *concentrated* acid, produces first a yellow and afterwards a crimson-red solution.

(9.) Paper is carbonized by the *strong* acid. If the acid be dilute, wet a piece of white paper at one spot and heat before a fire. As soon as the acid becomes sufficiently concentrated by evaporation, the paper will turn black.

Uses.—*In the arts and manufactures* the uses of the acid are numberless. *In medicine* the following preparations are officinal :—*Acidum Sulphuricum,* B.P., Sp. Gr., 1·84=96·8 per cent. of H_2SO_4 ; *Acidum Sulphuricum dilutum,* B.P., Sp. Gr., 1·394=13·64 per cent. of H_2SO_4 ; *Acidum Sulphuricum Aromaticum,* B.P., of similar strength to the dilute acid, but containing ginger and cinnamon.

Persulphuric Anhydride (S_2O_7).

Discovered by Berthelot. Prepared by passing silent electrical discharges for a long time through a mixture of equal volumes of sulphurous anhydride and oxygen.

Properties.—A syrupy liquid, solidifying at 32° F. (0° C.), decomposed more or less rapidly by water into H_2SO_4 and free oxygen, but undergoing instant decomposition in the presence of spongy platinum. It is a powerful oxidizing agent. Baric persulphate is soluble in water, but rapidly changes to the sulphate with evolution of oxygen.

Thiosulphuric Acid, $H_2S_2O_3=114$.

Synonyms.—*Hyposulphurous acid ; Sulpho-sulphuric acid ; Dithionous acid.*

The free acid has never been obtained. The salts are prepared either (1) by boiling sulphur in a solution of a sulphite ($Na_2SO_3+S=Na_2S_2O_3$) ; or (2) by boiling sulphur with an alkaline hydrate ($3CaO,H_2O+12S=CaS_2O_3+2CaS_5+3H_2O$). A further quantity of CaS_2O_3 may be formed from the CaS_5 in the latter reaction, by exposing the solution to the air ($CaS_5+3O=CaS_2O_3+S_3$).

Calcic Thiosulphate ($CaS_2O_3,6H_2O$) is found in large quantities in the refuse lime of gas works, and also in the refuse from the ball soda of the alkali works.

Sodic Thiosulphate [(Hyposulphite) ($Na_2S_2O_3,H_2O$ becoming $Na_2S_2O_3$ when dried at 482° F. (250°C.)] is largely used by the dyer as an antichlor to neutralise the injurious effects of any chlorine remaining in goods treated with bleaching powder. It is also employed in photography and metallurgy, on account of its power of dissolving the insoluble argentic haloid salts, by the formation of double soluble salts ($NaAgS_2O_3,H_2O$). It is prepared :—(1) By treating a solution of sodic sulphide with sulphurous acid, or (which is the same thing) by digesting together sulphur and sodic sulphite. In this reaction the sulphur, liberated by the action of the sulphurous acid on the alkaline sulphide, acts on the sodic sulphite also formed ($3H_2SO_3+2Na_2S=2Na_2SO_3+3S+3H_2O$). A thiosulphate results ($Na_2SO_3+S=Na_2S_2O_3$).

(2.) By heating a mixture of sulphur in a solution of caustic soda ($6NaHO+4S=Na_2S_2O_3+2Na_2S+3H_2O$).

(3.) By the action of iodine on a mixed solution of sodic sulphide and sulphite.

(4.) By exposing the calcic sulphide (tank waste or soda waste) of the gas or alkali works to the air, or by treating it with sulphurous acid. In these cases a calcic hyposulphite is formed by oxidation ($S_2Ca+3O=CaS_2O_3$), from which 'hyposulphite of soda' may be prepared by the action of sodic carbonate upon a solution of the lime salt.

The thiosulphates will not yield the free acid by the action of a stronger acid, on account of the ease with which they are decomposed into sulphur and sulphurous acid ($H_2S_2O_3=S+H_2SO_3$).

To distinguish thiosulphuric from sulphurous acid note that—

(1.) On adding an acid to a thiosulphate, sulphur is precipitated, and sulphurous anhydride is evolved.

(2.) Thiosulphuric acid dissolves argentic chloride, forming argentic sodic thiosulphite ($NaAgS_2O_3$).

(3.) A salt of ruthenium, rendered alkaline with ammonia, turns thiosulphuric acid a deep red color.

The sodic thiosulphate, when heated, first loses water, and is then decomposed ($4Na_2S_2O_3=3Na_2SO_4+Na_2S_5$).

Dithionous Acid, $H_2S_2O_4$ (formerly given as H_2SO_2).

Synonyms.—*Hydrosulphurous Acid; Hyposulphurous Acid.*

History.—Discovered by Schützenberger.

Preparation. (1.) By dissolving zinc in sulphurous acid. (Note :—No hydrogen is evolved during the reaction.)

$$\underset{\text{Sulphurous acid}}{2H_2SO_3} + \underset{\text{Zinc}}{Zn} = \underset{\text{Dithionous acid}}{H_2S_2O_4} + \underset{\text{Zinc oxide}}{ZnO} + \underset{\text{Water.}}{H_2O.}$$

Properties.—The yellow solution of the acid thus formed bleaches powerfully, its bleaching action depending on its reducing power. It throws down mercury and silver from their solutions. It rapidly decomposes in the air by absorbing oxygen ($H_2S_2O_4+O+H_2O=2H_2SO_3$).

It is employed as a laboratory reagent for estimating the free oxygen in drinking water.

Dithionic Acid, $H_2S_2O_6=162$.

Synonym.—*Hyposulphuric acid.*

Preparation. (α.) *A manganous dithionate* (MnS_2O_6) is first prepared by passing SO_2 through cold water containing manganese dioxide in suspension ($MnO_2+2SO_2=MnS_2O_6$).

(β.) *A baric dithionate* (BaS_2O_6) is then prepared by acting on manganous dithionate with baric sulphide ($MnS_2O_6+BaS=MnS+BaS_2O_6$).

(γ.) *Dithionic acid* is now liberated by the action of sulphuric acid on baric dithionate ($BaS_2O_6+H_2SO_4=BaSO_4+H_2S_2O_6$).

Properties.—The acid, when fully concentrated by evaporation 'in vacuo,' has a specific gravity of 1·347, and forms a colorless acid liquid without odor. If the concentration be attempted beyond this point, or if heat be applied to the acid solution, it breaks up into sulphuric acid and sulphurous anhydride ($H_2S_2O_6=H_2SO_4+SO_2$). When exposed to the air, dithionic acid is rapidly converted into sulphuric acid.

All the dithionates are soluble in water. They are decomposed by heat in the presence of hydrochloric acid, sulphurous anhydride being evolved *without the deposition of any free sulphur.* This distinguishes them from other sulphur compounds.

Trithionic Acid ($H_2S_3O_6$=194).

Synonyms.—*Dihydric trithionate; Sulphodithionic acid; Sulphuretted hyposulphuric acid.*

History.—Discovered by Langlois.

Preparation of the free acid. (*a.*) A potassic trithionate ($K_2S_3O_6$) is first prepared by digesting hydric potassic sulphite with sulphur :

$$\underset{\text{Hydric potassic sulphite}}{12KHSO_3} + \underset{\text{Sulphur}}{S_2} = \underset{\text{Potassic trithionate}}{4K_2S_3O_6} + \underset{\text{Potassic sulphite}}{2K_2SO_3} + \underset{\text{Water.}}{6H_2O}$$

(*β.*) On dissolving the crystals of potassic trithionate ($K_2S_3O_6$) in water, and adding perchloric or hydrofluosilicic acid to the solution, the potash is precipitated, and a solution of the acid obtained.

Properties.—The acid crystallizes in four-sided prisms. It rapidly decomposes into sulphurous anhydride, sulphurous acid, and free sulphur ($4H_2S_3O_6=6SO_2+4H_2SO_3+S_2$).

A sodic trithionate may be prepared by the action of iodine on a solution of sodic thiosulphate and sulphite. Sodium amalgam converts a trithionate into a mixed sulphite and thiosulphate.

The *trithionates* are soluble unstable salts, and are easily decomposed by heat into sulphates, sulphurous anhydride being evolved with the deposition of free sulphur. They give (1) with mercurous nitrate a *black* precipitate, (2) with mercuric nitrate a *white* precipitate, and (3) with argentic nitrate a *yellow* precipitate, which in time becomes black.

Tetrathionic Acid ($H_2S_4O_6$—226).

Synonyms.—*Dihydric Tetrathionate; Disulpho-dithionic acid; Bisulphuretted hyposulphuric acid.*

History.—Discovered by Fordos and Gélis.

Preparation of the free acid. (*a.*) Baric tetrathionate (or other salt) is formed by adding iodine to baric (or other) thiosulphate ($2BaS_2O_3+I_2=BaI_2+BaS_4O_6$).

(*β.*) *Tetrathionic acid* is set free by decomposing baric tetrathionate with its exact equivalent of sulphuric acid.

Properties.—The acid is very unstable. Sodium amalgam converts the tetrathionate into a hyposulphite. When heated, a solution of sulphuric acid is formed, sulphurous anhydride being evolved, and free sulphur deposited ($H_2S_4O_6=H_2SO_4+SO_2+S_2$). The potassic salt may be recognised by the separation of sulphur when heated with potassic sulphide ($2K_2S_4O_6+2K_2S=4K_2S_2O_3+S_2$).

Pentathionic Acid ($H_2S_5O_6=258$).

Synonyms.—*Trisulphodithionic acid; Trisulphuretted hyposulphuric acid.*

History.—Discovered by Wackenroder.

Preparation. (1.) By passing sulphuretted hydrogen into a solution of sulphurous acid ($10SO_2+10H_2S=2H_2S_5O_6+5S_2+8H_2O$).

(2.) By the action of sulphur chloride (S_2Cl_2) on baric thiosulphate ($S_2Cl_2+2BaS_2O_3=BaS_5O_6+BaCl_2+S$).

The clear solution is to be concentrated *in vacuo* over oil of vitriol.

Properties.—The solution thus obtained has a specific gravity of 1·6, and is acid, bitter and tolerably permanent. Concentrated beyond this gravity it rapidly decomposes. By heat it is resolved into sulphuric acid, sulphuretted hydrogen, sulphurous anhydride, and free sulphur ($2H_2S_5O_6=H_2SO_4+H_2S+4SO_2+2S_2$).

The polythionic acids, as an aid to memory, are represented by Bloxam as derived from oil of vitriol by successive additions of sulphurous anhydride and sulphur: thus

Oil of vitriol	H_2SO_4	$=H_2SO_4$
Dithionic acid	$H_2SO_4+SO_2$	$=H_2S_2O_6$
Trithionic ,,	$H_2SO_4+SO_2+S$	$=H_2S_3O_6$
Tetrathionic ,,	$H_2SO_4+SO_2+S_2$	$=H_2S_4O_6$
Pentathionic ,,	$H_2SO_4+SO_2+S_3$	$=H_2S_5O_6$

Note the following reactions with sulphuric acid:—

The *sulphates* with concentrated acid (hot or cold) emit no odor.

The *sulphites* with dilute acid (cold) emit an odor of SO_2.

The *dithionates* with dilute acid emit no odor in the cold, but when heated emit an odor of SO_2.

The *thiosulphates* with dilute sulphuric acid (cold) emit an odor of SO_2, free sulphur being deposited.

COMPOUNDS OF SULPHUR AND THE HALOIDS.

1. Chloride S_2Cl_2.	Bromide S_2Br_2.	Iodide S_2I_2.
2. Dichloride SCl_2.		
3. Tetrachloride SCl_4.		
4.		Hex-Iodide SI_6.

Sulphur Chloride (S_2Cl_2).

Molecular weight, 135. *Molecular volume,* $\boxed{|}$. *Specific gravity,* 1·68; *of vapor,* 4·7. *Boils at* 282·4° F. (139° C.).

Synonym.—*Disulphur dichloride.*

Preparation.—By passing dry chlorine into melted sulphur, and collecting the product in a dry cold receiver (direct union).

Properties.—A yellow volatile liquid (Sp. Gr. 1·68), fuming in the air, and emitting a pungent odor. The specific gravity of the vapor is 4·7. It is decomposed by water into sulphurous and hydrochloric acids, with free sulphur (electro-positive) ($2S_2Cl_2+2H_2O=4HCl+SO_2+3S$). It dissolves sulphur freely ; hence its use in the manufacture of vulcanised rubber. It acts powerfully on mercury.

Sulphur Dichloride ($SCl_2=103$).

Synonym.—*Hyposulphurous chloride.*

Preparation.—By saturating sulphur chloride with chlorine at 0° C.

Properties.—A deep red liquid. It is decomposed by heat and by water, and also by the sun's rays ($2SCl_2=S_2Cl_2+Cl_2$).

Sulphur Tetrachloride, $SCl_4=173$.

Synonym.—*Sulphurous chloride.*

This compound is not known in a free state, and there is some doubt even as to its existence in combination.

Preparation.—By saturating sulphur chloride with chlorine at —4° F. (—20° C.).

Properties.—A yellowish brown liquid—very unstable—decomposing above —4° F. (—20° C.) into SCl_2.

Sulphur Bromide (S_2Br_2) is a heavy red liquid formed by the direct union of the elements.

Sulphur Iodide (S_2I_2) is a dark grey solid produced by the direct union of the element under water with heat.

Sulphur Hexiodide (S_2I_6) is formed in crystals by evaporating a mixed solution of iodine and sulphur in carbon disulphide.

COMPOUNDS OF SULPHUR, OXYGEN AND THE HALOIDS.

Thionyl Chloride ($SOCl_2$).

Molecular weight, 119.

Synonym.—*Sulphurous oxydichloride.*

This is an analogous compound to SO_2, two of chlorine displacing one of oxygen.

Preparation.—By acting on sulphurous anhydride with phosphoric chloride. (Schiff.) ($PCl_5+SO_2=SOCl_2+POCl_3$.)

Properties.—A colorless, pungent liquid of great refractive power ; specific gravity, 1·675 ; boils at 172·4° F. (78° C.). It is decomposed by water into sulphurous and hydrochloric acids ($SOCl_2+2H_2O=H_2SO_3+2HCl$). It forms *thionamide* with ammonia.

Sulphuryl Dichloride (SO_2Cl_2=135).

Molecular volume, ☐☐. *Sp. gr.* 1·66. *Boils at* 158° F. (70° C.).

Synonym.—*Sulphuric oxydichloride.*

Preparation.—By exposing a mixture of sulphurous anhydride and chlorine to sunlight.

Properties.—A colorless liquid. Sp. gr., 1·66. Decomposed by a small quantity of water into sulphuric chlorhydrate (SO_3HCl) and hydrochloric acid, but by an excess of water into sulphuric and hydrochloric acids ($SO_2Cl_2+2H_2O=H_2SO_4+2HCl$).

Sulphuric Chlorhydrate (SO_3HCl).

This may be formed by the direct union of SO_3 and HCl, or by distilling a mixture of H_2SO_4 and PCl_5. It is a colorless liquid, and undergoes dissociation by heat. With water, sulphuric and hydrochloric acids are formed.

The Compound (SO_2ClO_2), called by Frankland *Pyrosulphurylic Chloride,* is formed by the action of phosphoric chloride or of sulphur chloride (S_2Cl_2) on sulphuric anhydride. It is a colorless liquid, decomposed by water into H_2SO_4 and HCl.

COMPOUNDS OF SULPHUR AND PHOSPHORUS.

P_4S	*Sulphur Tetraphosphide*	Both are oily liquids, and readily dissolve sulphur and phosphorus. They are prepared by melting sulphur and phosphorus together in atomic proportions.
P_2S	*Sulphur Diphosphide*	
P_4S_3	*Phosphorus Sesquisulphide*	All solid bodies, formed by direct union. P_4S_3 melts at 287·6° F. (142° C.), and decomposes when boiled in water to H_3PO_3, H_2S, and H_3P. P_2S_3 melts at 554° F. (290° C.), and is decomposed by water into H_3PO_3 and H_2S. P_2S_5 may be prepared by dissolving atomic proportions of sulphur and phosphorus in CS_2, heating the mixture in sealed tubes for some hours to 410° F. (210° C.) It is decomposed by water into H_3PO_4 and H_2S. It combines with alkaline sulphides to form sulpho-phosphates ($M'PSO_4$). It is used in the laboratory to replace oxygen by sulphur in organic compounds.
P_2S_3	*Phosphorous Sulphide*	
P_2S_4	*Diphosphoric Tetrasulphide*	
P_2S_5	*Phosphoric Sulphide*	
P_2S_{12}	*Phosphoric Dodecasulphide*	

Phosphoric Sulphochloride, $PSCl_3$.

Molecular weight, 169·5. *Specific gravity of liquid,* 1·631 *at* 68° F. (20° C.); *of vapor,* 5·878. *Boils at* 257° F. (125° C.).

Synonyms. — *Sulphotrichloride of Phosphorus ; Thiophosphoryl Chloride.*

Preparation.—(1.) By decomposing phosphoric chloride with sulphuretted hydrogen ($PCl_5 + SH_2 = PSCl_3 + 2HCl$).

(2.) By decomposing phosphoric chloride with phosphoric or antimonious sulphide ($3PCl_5 + Sb_2S_3 = 3PSCl_3 + 2SbCl_3$).

Properties.—A colorless, fuming liquid. When boiled with sodic hydrate, it forms sodic chloride and sodic sulphophosphate, from which the corresponding barium, calcium, and strontium salts may be prepared by double decomposition. (Wurtz.)

$$6NaHO + PSCl_3 = 3NaCl + Na_3PSO_3 + 3H_2O.$$

Sodic hydrate + Phosphoric sulphochloride = Sodic chloride + Sodic sulphophosphate + Water.

It is decomposed by water into phosphoric and hydrochloric acids, and sulphuretted hydrogen ($2PSCl_3 + 8H_2O = 2H_3PO_4 + 6HCl + 2H_2S$).

The bromine compound ($PSBr_3$) is analogous in its preparation and reactions to $PSCl_3$.

SELENIUM (Se_2).

Atomic weight, 79. *Molecular weight,* 158. *Molecular volume,* ☐☐ *Specific gravity of crystallized solid,* 4·788 ; *of vapor,* 5·68 ; *Atomicity, Hexad, Tetrad and Dyad.*

History.—Discovered by Berzelius (1817) in the refuse of a sulphuric acid factory (*σελήνη*, the moon).

Natural History.—It is found native, but occurs chiefly in combination, as a selenide of copper, lead, iron, silver, etc. It also occurs as an impurity in native sulphur (seleniferous sulphur).

Preparation.—By the action either of a mixture of nitric and sulphuric acids or of a solution of potassic cyanide on the seleniferous deposits of vitriol works, a solution containing selenious and selenic acids being formed. The selenic acid present in the solution is now reduced to selenious acid by the action of hydrochloric acid ($H_2SeO_4 + 2HCl = H_2SeO_3 + H_2O + Cl_2$). From this solution of selenious acid, the selenium may be precipitated by a current of sulphurous anhydride ($2H_2SeO_3 + 2H_2O + 4SO_2 = 4H_2SO_4 + Se_2$).

Varieties.—Like sulphur, selenium is found in various allotropic forms :—

(*α*.) The *amorphous form,* prepared as described above, consists of red flakes, which are ductile when melted. It has no taste or smell, and is a bad conductor of heat and electricity. It is soluble in carbon disulphide.

(*β*.) A *black vitreous form,* prepared by heating the amorphous variety (*α*) to 212° F. (100° C.), and then cooling rapidly. It has a specific gravity of 4·3. It is insoluble in carbon disulphide.

(*γ*.) A *crystalline form,* prepared by heating the vitreous form (*β*) to

204·8° F. (96° C.) The crystals are bluish grey (σελήνη, the moon). This change is accompanied by the evolution of great heat, the temperature rising above 392° F. (200° C.). Minute black crystals may also be prepared by exposing an alkaline selenide to the air. Crystal selenium has a specific gravity of 4·8. It is a conductor of electricity. Its electrical resistance is diminished by exposure to light, but is restored when the light is withdrawn. On this property the construction of the photophone depends. It is insoluble in carbon disulphide.

Properties.—(α.) *Physical.* The color of selenium is either red, black, or bluish grey, according to the variety. Solid selenium has neither taste nor smell, but the vapor has the odor of putrid horseradish. It is insoluble in water. It fuses readily at about 212° F. (100° C.), and boils at 1292° F. (700° C.), giving off a yellow vapor, which, like that of sulphur, expands anomalously (*see* page 174). Thus at 1580° F. (860° C.) it has a vapor density of 7·67, whilst at 2564° F. (1400° C.) its vapor density is 5·68.

(β.) *Chemical.* Selenium vapor burns with a blue flame, forming SeO_2. By boiling with nitric acid, selenious acid (H_2SeO_3) is formed. Selenium is soluble in sulphuric acid, forming a green solution, from which the selenium may be thrown down by the addition of water.

COMPOUNDS OF SELENIUM AND OXYGEN, ETC.

Selenious anhydride	SeO_2.
Selenious acid...	H_2SeO_3.
Selenic acid	H_2SeO_4.

Selenious Anhydride (SeO_2).

Preparation.—(1.) By burning selenium in oxygen.

(2.) By heating selenious acid.

Properties.—A white, deliquescent, crystalline substance, soluble in water, forming selenious acid (H_2SeO_3).

Selenious Acid (H_2SeO_3).

Preparation—(1.) By dissolving selenious anhydride in water.

(2.) By boiling selenium in nitric acid.

Properties.—This acid may be obtained as a white solid. On adding iron, zinc, sulphurous acid, or sulphuretted hydrogen to a solution of selenious acid, selenium will be precipitated ($H_2SeO_3+2H_2SO_3=2H_2SO_4+H_2O+Se$).

The acid forms normal, acid and super-acid salts.

Selenic Acid (H_2SeO_4).

This acid is not known as an anhydride.

Preparation.—(1.) (α.) *Potassic seleniate* is first formed by fusing together nitre and selenium ($4KNO_3+Se_2=2K_2SeO_4+2N_2O_2$). (β.) A *plumbic seleniate* is then prepared by the action of plumbic nitrate on a solution of potassic seleniate. (γ.) On treating plumbic seleniate with sulphuretted hydrogen, an insoluble plumbic sulphide is formed, together with a solution of selenic acid.

(2.) By the action of chlorine or of manganese dioxide on selenious acid, or by the action of bromine on argentic selenite suspended in water ($Ag_2SeO_3+Br_2+H_2O=H_2SeO_3+2AgBr$).

Properties.—A colorless, syrupy, hygroscopic liquid, evolving considerable heat when mixed with water. It may be concentrated until it has a specific gravity of 2·6, when it contains 97 per cent. of the acid. At a temperature of 554° F. (290° C.) it is decomposed into selenious acid, water, and oxygen. It has no action on platinum, but it oxidises the metals generally, and even (standing alone in this respect) dissolves gold. When heated with hydrochloric acid, it is decomposed ($H_2SeO_4+2HCl=H_2SeO_3+H_2O+Cl_2$).

Compounds of Selenium and Chlorine.

Selenium forms two chlorides, viz., a *monochloride* (Se_2Cl_2), a yellow liquid formed by the direct union of selenium and chlorine, and a *tetrachloride* ($SeCl_4$), a white crystalline solid, formed by treating Se_2Cl_2 with an excess of chlorine. On contact with moisture an *oxychloride* ($SeOCl_2$) is formed.

The combinations formed by selenium with the other haloid elements are very imperfectly understood.

A *carbon selenide* (CSe_2) and two *sulphides* (SeS_2 and SeS_3) have been described.

TELLURIUM (Te_2).

Atomic weight, 128 (?). [Mendeleef predicted that the atomic weight must be below the atomic weight of iodine (127). Recent experiments have shown that possibly 125 is the atomic weight of tellurium rather than 128.] *Molecular weight,* 256. *Specific gravity of solid* 6·2 ; *of vapor* (*at* 2,534° F.), 9·0. *Atomicity, hexad ; tetrad ; dyad.*

History.—Discovered by Müller von Reichenstein (1782). Its elementary nature was determined by Klaproth (1798), and the body named by him Tellurium (*Tellus*).

Natural History.—It is a very rare substance, but is found both in a free state, and combined with bismuth, lead, silver, etc., as tellurides.

Preparation.—By fusing bismuthic telluride (Bi_2Te_3) with carbon and sodic carbonate. The sodic telluride formed is dissolved in water and exposed to the air, when tellurium slowly deposits.

Properties.—(α.) *Physical.* A pinkish-white metallic-looking body, crystalline (rhombohedral), and very brittle. It fuses between 800° and 900° F. (426° and 482° C.), and may be distilled, becoming at a high temperature, a yellow gas. It conducts heat and electricity badly. It is insoluble in water. When taken internally it imparts a peculiar garlic odor to the breath.

(β.) *Chemical.* Tellurium burns, when heated in air, with a blue flame, yielding TeO_2. It does not form, like the metals, a true basic oxide. Its solution in sulphuric acid, which is of a purple-red color, yields a precipitate of tellurium when treated with water.

COMPOUNDS OF TELLURIUM AND OXYGEN, ETC.

Tellurous oxide or anhydride	TeO_2.
Telluric oxide or anhydride	TeO_3.
Tellurous acid	H_2TeO_3.
Telluric acid	H_2TeO_4.

Tellurous Oxide or Anhydride (TeO_2).

This oxide occurs native as tellurite. It is a white, fusible crystalline body. It forms a yellow glass when hot, which becomes white on cooling. At a greater heat it sublimes unchanged. It is slightly soluble in water, forming *tellurous acid* (H_2TeO_3).

Tellurous Acid (H_2TeO_3).

This acid is a white flocculent substance, decomposed into water and the anhydride at 104° F. (40° C.). It is a dibasic acid, and forms two classes of tellurites, viz.—*neutral* (M'_2TeO_8), and *acid* ($M'HTeO_3$).

Telluric Oxide or Anhydride (TeO_3).

Telluric oxide is prepared by the action of heat on *telluric acid* (H_2TeO_4). It is a yellow, solid body, insoluble in water and in cold acids. By treatment with boiling hydrochloric acid, tellurous oxide and free chlorine are formed ($TeO_3 + 2HCl = TeO_2 + H_2O + Cl_2$).

Telluric Acid (H_2TeO_4).

Preparation.—A potassic tellurate is formed by fusing tellurium with nitre. On adding baric chloride to a solution of the potassic tellurate, and decomposing the baric tellurate thus formed with sulphuric acid, a solution of telluric acid is obtained.

Properties.—The solution of the acid yields crystals having the composition $H_2TeO_4 + 2H_2O$, from which the two molecules of water may be expelled by heat. It forms salts called tellurates, which are mostly insoluble.

CHAPTER IX.

CARBON—BORON—SILICON.

CARBON:—Compounds of Carbon and Oxygen—Compounds of Carbon and the Haloids—Compounds of Carbon with Oxygen and the Haloids—Compounds of Carbon and Sulphur. BORON:—Boracic Acid—Compounds of Boron with Nitrogen, the Haloids, and Sulphur. SILICON:—Compounds of Silicon with Oxygen, the Haloids, Nitrogen, and Sulphur.

CARBON (C=12).

Atomic weight, 12. *Atomicity, tetrad* (CO_2—CH_4); *dyad* (CO). *Vapor density, unknown.*

Synonym.—*Charcoal.*

History.—Carbon has been known from very early times. Eresius (300 B.C.) described the method of preparing it from wood, and in Pliny's time it constituted the common fuel. In A.D. 1694 the Florentine academicians burnt the diamond by the sun's rays. In 1775-6 Lavoisier effected its combustion in oxygen, and in 1809 Davy burnt graphite in a similar manner. Thus these bodies respectively, were proved to be pure carbon. Newton, however, had, long before this, asserted that the diamond was a combustible body, on account of its high refractive power.

Natural History.—(α.) In the *mineral kingdom* carbon is found in a free state (1) as the *diamond* in sandstone rocks or mica slate. Its origin is unknown. The ash, consisting of silica and oxide of iron, left after its perfect combustion, is very minute. (2.) As *plumbago,* the ash of which varies from 2 to 5 per cent., and consists of a little quartz mixed with the oxides of iron and manganese. (3.) As *anthracite,* the ash of which varies greatly both in quantity and composition. (4.) Carbon is also found associated (*a*) with *hydrogen* in coal, bitumen, jet, shales, naphtha, and in the paraffines; (*b*) with *oxygen* in *carbonic anhydride,* and (*c*) with *oxygen and the metals* in the carbonates.

(β.) *In the vegetable kingdom,* carbon forms about 50 per cent. of dry vegetable solids. It is supplied to them by the atmospheric carbonic anhydride which the plant deoxidizes under the influence of solar light. Plants are *deoxidizing* agents, animals are *oxidizing* agents.

(γ.) *In the animal kingdom,* all tissues and products are largely made up of carbon. Fat contains about 79 per cent.

The chemist roughly proves a body to be of organic origin, by the circumstance that it carbonizes when burnt with a limited supply of air.

Varieties.—(1.) *Diamond.*—The diamond crystallizes in cubes or in octahedra with convex faces and rounded edges (lenticular). It cannot be produced artificially. Its specific gravity is 3·4. It is usually colorless, but is found at times of a yellow, green, blue, or black tint, the colors being due to mineral matter. It is one of the hardest bodies known (adamant). It has never been melted. It is a non-conductor of electricity, but when heated in the voltaic arc, it swells up and forms a coke-like mass, which conducts electricity freely. Some diamonds are phosphorescent after exposure to intense sunlight. It has a high refracting power; its limiting angle, that is, the angle at which all light is returned, being 24·1°.

It is not affected by the action of nitric acid and potassic chlorate. Unlike boron and silicon the diamond does not melt in fused aluminium.

A diamond may be known (α) by its *hardness* (scratching hardened steel); (β) by its *gravity;* and (γ) by its *insolubility* in *hydrofluoric acid.*

(2.) *Graphite* (γραφω, I write).—Graphite is found both crystalline (six-sided plates) and in amorphous masses. It has a specific gravity varying from 1·8 to 2·2. It is greyish-black, with a metallic lustre (*black lead* or *plumbago*). It is unctuous to touch, and, although the minute particles are excessively hard, it nevertheless marks paper when drawn across it. It is a good conductor of electricity.

When plumbago is acted on with a mixture of nitric acid and potassic chlorate it forms '*graphic* or *graphitic acid*' ($C_{11}H_4O_5$) a brown, crystalline body, which swells up and often explodes when heated, forming '*pyrographitic oxide* ($C_{22}H_2O_4$). This latter substance is soluble in a mixture of nitric acid and potassic chlorate.

(3.) *Amorphous carbon.*—Amorphous carbon has a specific gravity varying from 1·6 to 2·0. Its apparent lightness, such as floating on water, is due to the presence of air in its pores. It is found in various forms, more or less pure, as *e.g.* (α.) *Coke,* the residue of coal after the gas and volatile matters have been expelled. (β.) *The carbon of gas retorts;* a body resembling graphite in some particulars, but differing in that it does not form "graphic acid" by the action of nitric acid and potassic chlorate. (γ.) *Soot,* the condensed smoke deposited in chimneys. (δ.) *Lampblack,* the unburnt carbon resulting from the combustion of rich hydro-carbons in a limited supply of air. (ε.) *Wood charcoal,* the carbon of wood and other vegetable matters. (ζ.) *Animal charcoal* (*ivory black* or *bone black*), the carbon of bone or other animal substances. (η.) *Tinder.*

All these forms, when treated with a mixture of nitric acid and potassic chlorate, yield brown compounds that are soluble in water.

It has been conjectured, considering the striking differences in the properties of these carbon allotropes, that they consist of dissimilar carbon molecules. The study of their specific heats would suggest that the charcoal molecule consists of two atoms, the graphite of three, and the diamond of four. (Specific heat of *diamond*, 0·1128 at 10° C. and 0·4589 at 985° C.; of *plumbago*, 0·1437 at 10° C.; of *charcoal*, 0·2415.)

Preparation.—(1.) *Diamond.*—The diamond is the only allotrope of carbon that cannot be prepared artificially.

(2.) *Graphite.*—(*a.*) By submitting the diamond or amorphous carbon to the intense heat of the electric arc in an atmosphere free from oxygen.

(*β.*) By dissolving carbon in cast iron. On allowing the mixture to cool slowly, six-sided crystalline plates of graphite (called "kish") are formed. The insoluble graphitic carbon may be separated by dissolving the iron in an acid.

(3.) *Amorphous carbon.*—(*a.*) *Coke.* By heating coal in closed iron cylinders, an escape being provided for the gaseous and other volatile matters. The higher the temperature to which the coal is subjected, the more dense the coke. Coke may also be prepared by burning the coal in heaps, in similar manner to the preparation of wood-charcoal. Most of the coke used in metallurgical operations is prepared in specially constructed coking ovens, which yield a denser article than that obtained by other means. Coke in burning gives no smoke and great heat.

(*β.*) *Carbon of gas retorts.*—From the decomposition of a portion of the gas or volatile hydro-carbons by the intensely heated retort, upon which a layer of gas carbon slowly deposits. Its appearance varies somewhat according to the temperature at which it is formed.

(*γ.*) *Soot.*—The condensed smoke of chimneys.

(*δ.*) *Lampblack.*—By burning certain vegetable matters rich in carbon, such as resin, tar, etc., in a current of air insufficient for complete combustion. The hydrogen, being the most combustible portion, burns first, and the carbon, for which there is not sufficient air, is collected in chambers covered with coarse canvas. To free it from hydrogen, the lampblack should be strongly heated in a current of chlorine.

(*ε.*) *Wood charcoal.*—(1.) By the distillation of dry wood in closed cast iron retorts, the wood being placed in a perforated iron case (slip). *Acid* fumes are evolved during the process. If damp wood be used, the water will be decomposed and a loss of carbon result from the formation of $CO + CO_2$. The acid fumes are condensed, acetic acid and wood naphtha being by this means recovered. (2.) By the slow burning of logs of *dry* wood arranged in heaps, covered, except round the base of the heap, with turf. In this way, every 100 parts of wood yield about 22 parts of carbon.*

Wood charcoal never consists of pure carbon. The higher the temperature at which the wood is burnt, the smaller the quantity of charcoal formed, but the larger the percentage of carbon that it contains. The "charbon roux" of the French consists of wood imperfectly burnt by the action of superheated steam.

(ζ.) *Animal charcoal* (*ivory black*).—By burning bones or other animal matters in closed retorts. A fetid oil is given off together with *alkaline* fumes, the nitrogen present forming ammonia.

(η.) Carbon is set free by the action of potassium on a carbonate or on carbonic acid at a high temperature ($2K_2 + 3CO_2 = C + 2K_2CO_3$).

Properties.—(α.) *Sensible.*—Carbon, in all its forms, is a solid, without taste or smell. Excepting the diamond, all varieties are black.

(β.) *Physical.*—Carbon in the form of diamond is the hardest substance known, although in this respect nearly approached by crystallized boron. The other varieties are comparatively soft, although graphite, which may be easily cut with a saw, is said to wear out the instruments rapidly, owing to the extreme hardness of its minute particles.

Carbon is *dimorphous.* It is *cubic* in the diamond, and *six sided* in some varieties of graphite. The other forms of carbon, as well as occasionally graphite, are amorphous. Its specific gravity varies; that of the *diamond* ranges from 3·33 to 3·55; of *graphite*, from 2·0 to 2·35; of *anthracite* and *coke*, from 1·4 to 2, etc.

Action of heat.—Carbon, in all its forms, is believed to be infusible and non-volatile. It has been noticed, however, that when the carbon points from a large battery are brought into contact in an exhausted receiver, a dark cloud appears, being a black crystalline body slowly deposited on the sides of the glass. Further, finely powdered carbon after exposure to the intense heat of the voltaic arc, forms a coherent mass as if it had been fused. (Despretz.) The diamond, when heated in the battery, swells up and cakes, although there is no reason to believe that it is capable of vaporisation. Finely-divided carbon conducts heat badly. The diamond is a non-conductor of heat. The other varieties of carbon when "en masse," conduct heat well, their power of conduction increasing with density.

---

* If a piece of wood ($C_6H_{10}O_5$) be burnt in the *open fire*, with free access of air, carbonic acid and water only are produced; but when burnt in a *close vessel*, *i.e.*, where free access of oxygen is prevented, the wood does not truly burn, but simply undergoes destructive distillation; that is, it becomes changed into simpler and more stable products, tar, acetic acid, and wood spirit being amongst the products formed.

Carbon, in all forms, excepting that of the diamond, is a conductor of electricity. Hence the use of graphite in electrotyping.

(γ.) *Chemical.*—Carbon in all varieties is combustible in air and oxygen, yielding as its sole product carbonic anhydride (CO_2). The diamond and graphite are difficult of combustion, but the rest burn easily. In none of its forms is carbon altered by exposure to air ; hence many of its uses.

Action of oxygen.—The action of oxygen on carbon is sometimes, though rarely, manifested at ordinary temperatures. Thus ferric may be changed to ferrous, and mercuric to mercurous salts, by merely shaking up their solutions with powdered charcoal. At high temperatures, carbon burns in oxygen, and even in carbonic anhydride, in which latter it appropriates one half of the oxygen ($C+CO_2=2CO$.) Hot charcoal decomposes steam, liberating hydrogen, and setting free, according to the temperature, either carbonic anhydride or carbonic oxide. Its property of combining with oxygen is made use of in extracting the metals from their oxides, carbonic anhydride being set free in the case of easily reduced oxides ($2PbO+C = Pb_2+CO_2$), and carbonic oxide in the case of those more difficult of reduction ($ZnO+C = Zn+CO$.)

Action of the haloids.—The direct combination of carbon with the haloids cannot be effected, but indirect combination, either by the substitution of the haloid elements for hydrogen in, or the addition of the haloid elements to, the hydrocarbons, is of constant occurrence. Thus ethylene (C_2H_4) will combine with bromine to form ethylene dibromide ($C_2H_4Br_2$), which, by successive substitutions of bromine for hydrogen, may ultimately be converted into tetrabromethylene dibromide (C_2Br_6).

A solution of chlorine appears to dissolve animal charcoal, but this apparent solubility is simply oxidation, CO_2 being given off. A similar result occurs with nitric acid.

Action on nitrogen.—The direct union of carbon with nitrogen cannot be effected ; but if nitrogen be passed over a mixture of carbon and potassic carbonate heated to redness, cyanogen (CN) is formed, which by its union with potassium forms potassic cyanide ($K_2CO_3+4C+N_2 = 2KCN+3CO$.)

Action on sulphur.—Direct union between carbon and sulphur occurs at a high temperature, carbonic disulphide (CS_2) being formed.

Action on hydrogen.—Hydrogen unites directly with carbon at high temperatures, such as the heat of the voltaic arc, forming acetylene (C_2H_2). (Berthollet.) During the destructive distillation of organic bodies, numerous hydrocarbons are produced. (*See* DESTRUCTIVE DISTILLATION.)

Action on the metals.—Carbon unites at high temperatures with certain metals, such as iron, manganese, palladium, iridium, etc., forming carbides.

Carbon does not combine with phosphorus.

We may note generally, that carbon exhibits a great indisposition to combine directly with the elementary bodies. Air and water have also but little action upon it. Hence it is customary to char the ends of stakes in order to prevent their decay by the action of air and moisture when driven into the ground, and to black-lead metal to prevent its oxidation.

Action of Compounds.—(1.) *Water* has no action on carbon, except the carbon be red-hot, when hydrogen, together with carbonic oxide or carbonic anhydride (one or both), are formed ($3H_2O + 2C = 3H_2 + CO + CO_2$).

(2.) *Acids.*—*Sulphuric acid* has no action on carbon, unless the mixture be heated, when the acid is reduced ($2H_2SO_4 + C = CO_2 + 2SO_2 + 2H_2O$). *Nitric acid* deflagrates when heated with carbon, the oxides of carbon and the lower oxides of nitrogen being formed. The action of nitric acid with potassic chlorate on the various forms of carbon is as follows :—Diamond is unaffected ; graphite is changed into graphic or graphitic acid (graphitic oxide) ($C_{11}H_4O_5$), a yellow silky substance, insoluble in water or in acids, and which, when heated, swells up, and becomes pyrographitic oxide ; the amorphous varieties are soluble, forming brown solutions. *Hydrochloric* and *hydrofluoric acids* have no action on carbon. *Phosphoric* acid is reduced by it, phosphorus being set free.

(3.) *The fixed alkalies* and the *oxides* generally do not act on carbon unless the carbon be heated, when the metals are reduced.

Red-hot carbon decomposes *ammonia,* forming ammonic cyanide, hydrogen, and nitrogen.

Charcoal has certain remarkable properties of absorption, which we must consider :—

(*a.*) *Its power of absorbing aqueous vapor.*—Recently ignited charcoal from different sources was found to absorb the following percentages, by weight, of *water* (Allen and Pepys) :—

	Weight of H_2O per cent. absorbed.
Lignum vitæ charcoal	9·6
Fir charcoal	13·0
Beech charcoal	16·0
Oak charcoal	16·5
Mahogany charcoal	18·0

(*b.*) *Its power of absorbing gases.*—The more liquefiable the gas, the more easily it would seem to be absorbed. A piece of *hard wood charcoal* was found to absorb gases in the following proportions :—

	Volume of gas absorbed.
Ammonia (NH_3)	90
Hydrochloric acid	85
Sulphurous anhydride	65
Sulphuretted hydrogen (H_2S)	55
Nitrous oxide (N_2O)	40
Carbonic acid (CO_2)	35
Carbonic oxide (CO)	9·4
Oxygen	9·3
Nitrogen	7·5
Hydrogen	1·75

Charcoal made from the shell of the cocoa-nut is said to be the most absorbent of all varieties. (Dewar.)

(*c.*) *Its power of absorbing odors.*—The deodorizing property of charcoal is very marked. Hence its supposed antiseptic properties. It does not, however, prevent decomposition, but absorbs noxious gases, afterwards oxidizing them by the oxygen condensed in the pores (Stenhouse), dissipating the carbon of the noxious matters as carbonic acid, and the hydrogen as water. The ammonia formed is absorbed by the charcoal.

(*d.*) *Its power of absorbing coloring matters.*—The decolorizing property of charcoal is specially manifested in the case of *animal charcoal* or bone-black, possibly because it contains a large proportion of calcic phosphate, which serves to extend the carbon particles. Hence its use in sugar factories. After the decolorizing power is exhausted it may be renewed by reheating the carbon in closed vessels. Seaweed charcoal has also very considerable decolorizing power.

(*e.*) *Its power of absorbing mineral and other substances.*—Thus, if strychnia or iodine in solution be shaken up with charcoal, they are rapidly absorbed. Lime may be abstracted from lime water, and lead acetate from its solution by similar treatment. Charcoal is used by the distiller for the purpose of removing the empyreumatic oils from spirit.

Uses. (A.) IN NATURE.—Carbon is found as a constituent of every organic substance. Thus it gives the plant its solidity and its form. Organic chemistry has been defined as the chemistry of carbon and its compounds.

(B.) IN THE ARTS. (*a.*) *Diamonds* are used (1) as *gems;* (2) for *glass cutting;* and (3) for *lapidary work.* The diamond dust commonly used for this purpose is the powder of the dark Brazilian diamond.

(*β.*) *Graphite* is used (1) for *pencils* (black lead); (2) for *black-leading* to protect iron from rust; (3) for *crucibles* mixed with clay (blue pots) on account of its power of resisting high temperatures and sudden changes ; (4) as a *lubricator* to diminish the friction of machinery ; (5) as a facing or *protectant* for gunpowder, etc.

(γ.) *Coke* is used for domestic firing and in metallurgical operations.

(δ.) *Gas Carbon* is a good conductor of electricity. It is used for battery plates, for the carbon of arc lights, etc.

(ε.) *Lamp Black*, owing to its unalterable nature, is used as a *pigment* in the manufacture of printing ink, blacking, etc.

(ζ.) *Vegetable or wood charcoal* is used as a *disinfectant* and *deodorizer*. Thus, in *covering graves*, in *dissecting rooms* and in hospital wards it is used to prevent offensive smells being emitted from putrescent matters, whilst in *respirators* it is employed to purify a vitiated air before it reaches the lungs. (Stenhouse.)

(η.) *Animal charcoal* is largely used as a *decolorizer* in sugar-refining, in the purification of alkaloids, oils, etc.

(θ.) *As an absorbent of impurities*, we employ animal charcoal for water filters, whilst in cases of poisoning by various substances, such as strychnia, etc., the injection of charcoal into the stomach as an absorbent constitutes an important method of treatment.

(ι.) *As a fuel* the use of charcoal is important.

Coal.

Coal has a vegetable origin. The change from wood to coal is effected by a peculiar decomposition or fermentation, brought about by the agency of heat and moisture under great pressure with exclusion of air, whereby much of the *hydrogen* of the wood is eliminated as marsh gas (CH_4), and the *oxygen* as carbonic anhydride (CO_2), an accumulation of the carbon resulting. These changes, from wood to anthracite, the oldest of the carboniferous deposits, are represented in successive steps in the following table :—

	Carbon.	Hydrogen.	Oxygen.
(1.) Wood	100	12·18	83·07
(2.) Peat	100	9·85	55·67
(3.) Lignite	100	8·37	42·42
(4.) Bituminous coal ...	100	6·12	21·23
(5.) Anthracite	100	2·84	1·74

The passage from wood to coal, therefore, consists in the storage of the carbon and in the elimination of the hydrogen and oxygen. A little sulphur is also present in coal, derived partly from vegetable albumen, and partly existing as FeS_2 derived from extraneous sources. There are also certain saline and earthy substances present, which constitute the coal ashes.

The composition of various kinds of coal is shown in the following table :—

	Lignite. Brown Coal.	Bituminous Coal.	Wigan Cannel.	Anthracite.	Coke.
Carbon	66·32	78·57	80·06	90·39	96·6
Hydrogen ..	5·63	5·29	5·53	3·28	0·4
Nitrogen ..	0·56	1·84	2·12	0·83	0·1
Oxygen	22·86	12·88	8·09	2·98	0·8
Sulphur	2·36	0·39	1·50	0·91	0·3
Ash	2·27	1·03	2·70	1·61	1·8
	100·00	100·00	100·00	100·00	100·0

The ash of coal varies, however, to a much greater extent than is stated above. A good coal should not contain more than 5 per cent. of ash, whilst a bad coal often contains 25 per cent. The following is the average percentage composition of 40 samples of ash:—

Silica	44·8
Lime	9·9
Magnesia	2·4
Alumina and ferric oxide ...	33·7
Sulphuric acid	8·4
Phosphoric acid	0·8
	100·0

The *sulphur* present in the coal is important, the product of its combustion being sulphurous acid. Good coal should not contain more than from 1 to 1·5 per cent. of sulphur. The coke, which varies from 50 to 70 per cent. of the coal carbonized, generally contains about one-half the quantity of the sulphur present in the coal from which it was prepared.

Amount of Sulphur in different Varieties of Coal.

	Maximum.	Minimum.	Average.
Welsh	5·07	0·09	36 exps. 1·47
Newcastle	2·85	0·06	18 ,, 1·24
Derbyshire	1·30	0·80	7 ,, 1·01
Lancashire	3·04	0·52	28 ,, 1·43
Scotch	1·57	0·33	8 ,, 1·11

When coal is heated *in closed vessels*, the volatile ingredients, as well as the hydrogen, oxygen, and nitrogen present in the coal, are driven off, either in a free state or combined with more or less carbon, whilst coke (that is, the carbon and earthy matter) remains in the retort. The composition of coke will be seen in the above table. The more intense the heat to which the coal is subjected, the more dense and the more incombustible the coke, and the better fitted it becomes for producing a steady and intense heat.

Process of burning coal in the open fire.—When the coal is heated it first softens, then swells up, and finally gives off certain gaseous products (such as CH_4 and C_2H_4), which take fire. If sufficient oxygen be present, all the carbon would be dissipated as CO_2, and all the hydrogen as H_2O. This, however, never happens in a fire grate. Such gases as CH_4 and C_2H_4 (marsh and olefiant gas) burn without smoke. A large quantity of hydrocarbon vapors, however, such as benzol, naphthalene, etc., which are also formed, catch fire, but the oxygen being present in insufficient quantity, these undergo only partial combustion. The unconsumed carbon from these bodies, together with ammonic carbonate and other products, escape to form the *smoke* and *soot*. The hot coke now left in the grate burns away until all the carbon is consumed, and the ash or incombustible mineral matter only remains.

When coke is used as a fuel, it does not undergo the first changes just described. Coke does not swell or soften, and for this reason cannot choke the draught like coal. Further it is less combustible than coal, from the absence of inflammable hydrocarbons, and consequently burns without smoke.

It will be noted that *anthracite* or *steam coal* (stone coal or Welsh coal), contains more carbon and less hydrogen than ordinary coal. It, in fact, more nearly approaches the condition of coke. It therefore emits, when burnt, but little smoke and but little volatile matter, and consequently but little flame. Its principal use is for furnaces.

Smoke nuisances.—To remedy or reduce to a minimum the escape of smoke, three things are necessary :

1st. That the fuel should be supplied in small quantities at a time, and be placed well in front of the fire. (In Jucke's patent a regular supply of fuel is effected by mechanical means.)

2nd. That a strong fire should be constantly maintained.

[The fuel should be supplied in *small quantities*, in order that the volatile hydrocarbons should not be evolved in too great abundance at a time ; and it should be put *in front of the fire*, so that before their escape they may pass over a large surface of glowing embers, whilst it is important that the *fire should be burning briskly*, in order that the gases and vapors may be consumed as fast as they are generated.]

3rdly. There should be an adequate supply of air. In certain smoke preventers (as Hill's patent) hot air is supplied to the gases as they leave the fire, in order to complete the combustion of any unburnt portions.

It is clear that the prevention of smoke depends largely on the attention of the stoker.

Charcoal is often used as fuel. Its advantage over wood is twofold ; (1) That the moisture and volatile matters of the wood have been got rid of ; and (2) that the percentage quantity of carbon is much greater in the charcoal than it is in the wood. In the first case much heat is lost in the formation of steam and volatile compounds when wood is used for fuel, which is avoided by using charcoal ; and in the second case, a given weight of charcoal emits twice as much heat as the same weight of wood. Thus the use of charcoal both prevents loss and concentrates heat.

(C.) In Medicine charcoal has been employed in cases of dyspepsia, obstinate constipation, and as an application to foul ulcers [carbo animalis, B.P. (bone-black)]. The charcoal is purified (carbo animalis purificatus, B.P.) by digesting the crude charcoal in hydrochloric acid and water to remove the calcic phosphate. Carbo ligni, B.P., (wood charcoal,) is also officinal. It is often administered in the form of biscuits or lozenges. Its use in various cases of poisoning has been already noticed.

COMPOUNDS OF CARBON AND OXYGEN.

Carbonic oxide	CO.
Carbonic anhydride	CO_2.

Carbonic Oxide, CO.

Molecular weight, 28. *Molecular volume*, ☐☐ . *Relative weight*, 14. *Specific gravity*, 0·967. *Calculated* (0·0693 × 14) 0·970. 1 *litre weighs* 1·254 *grms., and* 100 *cubic inches*, 10·002 *grains*.

Synonyms.—*Carbon monoxide.*

History.—Discovered by Priestley when igniting chalk in a gun-barrel. He supposed it to be hydrogen. Its true nature was afterwards determined (1803) by Cruickshank, Clement, and Desormes.

Natural History.—It is never found except as an artificial product, as *e.g.*, (1.) In the neighbourhood of *brick* or *lime kilns* ; (2.) In the gases issuing from *iron blast-furnaces* (25 to 32 per cent.), from *copper refining furnaces* (15 per cent.), as well as from ordinary stoves. Its escape means waste.

Preparation.—(1.) By burning carbon in a limited supply of air. (2.) By passing carbonic anhydride over either red-hot iron (Priestley) or red hot carbon, or by heating a carbonate (other than an alkaline carbonate) with iron filings or charcoal :—

(α.) $4CO_2 + Fe_3 = Fe_3O_4 + 4CO.$
Carbonic anhydride + Iron = Magnetic oxide of iron + Carbonic oxide.

(β.) $CO_2 + C = 2CO.$
Carbonic anhydride + Carbon = Carbonic oxide.

(γ.) $CaCO_3 + C = CaO + 2CO.$
Calcic carbonate + Carbon = Lime + Carbonic oxide.

(3.) By heating together oxalic acid (or an oxalate) and sulphuric acid:—

$C_2H_2O_4 + H_2SO_4 = CO_2 + CO + H_2O + H_2SO$
Oxalic acid + Sulphuric acid = Carbonic anhydride + Carbonic oxide + Water + Sulphuric acid.

[NOTE.—1. The sulphuric acid merely abstracts water from the oxalic acid.

2. By washing the gaseous products with a solution of sodic hydrate, the CO_2 will be dissolved and the CO be left.]

(4.) By heating together potassic ferrocyanide and sulphuric acid :—

$K_4FeC_6N_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$
Potassic ferrocyanide + Sulphuric acid + Water = Potassic sulphate + Ferrous sulphate + Ammonic sulphate + Carbonic oxide.

(5.) By heating a formate (or formic acid) with sulphuric acid :—

$CH_2O_2 = H_2O + CO.$
Formic acid = Water + Carbonic oxide.

(6.) By heating ferric or zinc oxide with charcoal :—

$ZnO + C = Zn + CO.$
Zinc oxide + Carbon = Zinc + Carbonic oxide.

Properties.—(α.) *Sensible.*—A colorless gas without odor or taste.

(β.) *Physiological.*—Carbonic oxide is a pure narcotic poison. Its effects were described by Guyton Morveau in 1802, and by Sir H. Davy in 1810. Its injurious effects, when injected into the veins, were recorded by Nysten. Tourdes proved that 1 part of the gas in 7 of air killed rabbits in seven minutes, 1 in 15 in twenty-three minutes, and 1 in 30 in thirty-seven minutes. Leblanc and Dumas' experiments show that air containing 1 per cent. of the gas will kill a dog in one and a-half minutes, and that birds die instantly in an atmosphere containing 5 per cent.

Dr. Letheby found in his experiments that air containing 0·5 per cent. of the gas kills small birds in about three minutes, whilst an atmosphere containing 1 per cent. proves fatal in about half the time.

It has been proved that the poisonous action of carbonic oxide depends on the formation in the blood of a new and fixed compound of carbonic oxide and hæmoglobin.

(γ.) *Physical.*—Its specific gravity is 0·967; the gas, therefore, is fourteen times heavier than hydrogen. At—310° F. (—190° C.), at ordinary pressure, the gas has been liquefied, and at—349·6° F. (—212° C.) solidified. Its "critical point" (*see* p. 213) is —179·1° F.

(−139·5° C.). Pressure without cold has as yet failed to liquefy it. It is decomposed, when passed through a red-hot tube, into carbon and carbonic anhydride. (*See* page 15.) It is slightly soluble in water and alcohol, 100 volumes of water dissolving 2·43 volumes at 60° F., and 100 volumes of alcohol 20 volumes of the gas.

(δ.) *Chemical.*—Carbonic oxide is an indifferent oxide, and has no action, free or dissolved, either on litmus or turmeric. It burns with a pale blue and very hot flame, carbonic anhydride being the only product. It neither supports combustion, nor whitens lime water. It explodes with half its volume of oxygen, forming carbonic anhydride. It has no action on any metal, except potassium, which absorbs it when heated to 176° F. (80° C.) (K_2CO). It combines with chlorine in equal volumes under the influence of sunlight to form phosgene gas ($COCl_2$).

It forms potassic formate when heated with potassic hydrate ($KHO + CO = KCHO_2$). It is absorbed by a solution of cuprous chloride in hydrochloric acid, forming the compound ($CO,Cu_2Cl_2,2H_2O$). On boiling this liquid, the CO is expelled unaltered.

The carbonic oxide flame is employed in the reverberatory furnace as a reducing agent, where it is made to play over metallic ores, the CO becoming CO_2 at the expense of the oxygen of the metallic oxide. The carbonic oxide is produced by causing the carbonic anhydride, formed at the bottom of the grate, to pass through the hot coal in the grate ($CO_2 + C = 2CO$). The same thing occurs in an ordinary stove, the CO_2 formed at the bottom of the stove where there is plenty of air, becoming CO as it passes through the fire, which burns so soon as it reaches the surface. Carbonic oxide is present to the extent of 34 per cent. in water gas. This is prepared by first passing steam over red-hot coke, whereby hydrogen and carbonic oxide are formed ($4H_2O + C_3 = CO_2 + 2CO + 4H_2$), the combustible gases being afterwards rendered illuminating, by causing them to traverse red-hot coke saturated with melted resin. The presence of so large a quantity of carbonic oxide would render the use of water gas very dangerous. Common coal gas also contains from 4 to 7 per cent. of carbonic oxide. As a fact carbonic oxide always results from the destructive distillation of organic bodies containing oxygen.

Carbonic Anhydride CO_2.

Molecular weight, 44. *Molecular volume,* $\boxed{\quad}\boxed{\quad}$. *Specific gravity,* 1·529 : *Calculated* (0·0693 × 22) 1·524. 100 *cubic inches weigh* 47·146 *grains, and* 1 *litre* 1·971 *grms.*

Synonyms.—Commonly called *Carbonic acid; Carbon or Carbonic Dioxide; Mephitic Air; Gas Sylvestre; Fixed Air* (Black); *Choke Damp.*

History.—Carbonic anhydride was known to Paracelsus and Von Helmont. It was examined by Black in 1757, and called by him

'Fixed Air.' In 1775 Lavoisier, by careful experiments on the product of the combustion of the diamond, determined its exact nature and named it carbonic acid.

Natural History.—(*a.*) *In the mineral kingdom* carbonic anhydride is found *free* in the air to the extent of about 0·04 per cent. It is evolved—

(1.) *As a product of respiration in man and animals.*—Respired air contains about 4 per cent. of carbonic anhydride, produced by the slow oxidation of the tissues.

(2.) *As a product of fermentation.*—Thus, accidents have arisen from plunging the head into fermenting vats.

(3.) *As a product of lime burning.*—Calcic carbonate when heated evolves carbonic anhydride, leaving caustic lime ($CaCO_3 = CaO + CO_2$). In volcanic districts a similar action takes place by subterranean heat; thus immense quantities of CO_2 are given out into the air, whilst the springs in the neighbourhood become charged with the gas.

(4.) *As a product of slow oxidation.*—Thus, spring water becomes impregnated with carbonic acid from the oxidation of the organic matter by the oxygen dissolved in the water. If a bottle half full of water containing organic matter, be kept in a warm room and in a closed vessel, the oxygen in the bottle will be found after a time to be more or less completely replaced by a corresponding volume of carbonic anhydride. So also carbonic anhydride no doubt results during the formation of coal, just as it is found in old wells and cellars, where it is produced by the decay of organic matter and in some cases, perhaps, exhaled from the earth.

(5.) *As a product of the explosion of fire-damp* (CH_4).—The poisonous action of the product of the explosion of fire-damp, viz. carbonic anhydride (*choke damp*), is more often the cause of fatal accident than the explosion itself.

(6.) *As a product of combustion.*—All bodies containing carbon yield by combustion carbonic anhydride. Two ordinary candles produce as much carbonic anhydride in an equal time as one adult. (Angus Smith.)

It is also found in a combined state in carbonates, as in limestone, marble, and chalk.

(*β.*) It is not found in any great quantity in the *vegetable kingdom*, the special action of the plant being to decompose it, whilst (γ) in *the animal kingdom* it is found in the exhaled air derived from the combustion of tissue.

Preparation.—(1.) By burning carbon in air or in oxygen ($C + O_2 = CO_2$).

(2.) By the action of acids on carbonates. If sulphuric acid be poured on marble, carbonic anhydride is set free, but the action is soon arrested by the formation of an insoluble lime sulphate over the surface of the marble. (Chalk with dilute sulphuric acid can be used.)

Hence we ordinarily employ HCl for the purpose of liberating the gas :—

$$\underset{\text{Calcic carbonate}}{CaCO_3} \;+\; \underset{\text{Hydrochloric acid}}{2HCl} \;=\; \underset{\text{Calcic chloride}}{CaCl_2} \;+\; \underset{\text{Water}}{H_2O} \;+\; \underset{\text{Carbonic anhydride}}{CO_2}.$$

It must be collected by displacement.

(3.) By heating carbonates other than alkaline carbonates :— ($CaCO_3 = CaO + CO_2$).

Properties.—(*a.*) *Sensible.* Carbonic anhydride is a colorless gas. It has no odor when largely diluted with air, but the presence of above 5 per cent. of CO_2 renders the air irritating and pungent.

(*β.*) *Physiological.* When *swallowed*, the gas is harmless. When inhaled it acts as a narcotic poison.

(1.) The *undiluted* gas kills instantly by causing spasm of the glottis.

(2.) When *diluted* with air, so that the proportion of the gas present is about 12 or 14 per cent. (as occurs in a room where a chafing dish has been burnt) it causes giddiness, hurried circulation, fulness in the head, noises, confusion, perhaps delirium, and finally coma, which may last a considerable time.

(3.) Air containing 4 or 5 per cent. of carbonic anhydride (such as air once breathed) causes a sense of oppression with headache, distress, and perhaps delirium or coma.

(4.) Air containing 3 per cent. of carbonic anhydride cannot be breathed without great distress, and will probably produce insensibility.

(5.) An atmosphere containing 1 or even 0·5 per cent. of carbonic anhydride (such as is found in ill-ventilated theatres) is distressing.

(6.) Its presence in the proportion of 0·1 per cent. may be considered the boundary line between good and bad air.

These facts show the necessity of good ventilation. Although carbonic anhydride is half as heavy again as air, nevertheless the processes whereby it is produced render it specifically lighter by raising its temperature. Thus it *ascends* and accumulates near the ceiling. The chimney opening only ventilates the lower part of the room.

(*γ.*) *Physical.* The specific gravity of carbonic anhydride is 1·529, that is, it is 22 times heavier than hydrogen. Hence it accumulates on the floors of caves and caverns (Grotto del Cane). By a pressure of 50 atmospheres at 59° F. (15° C.), or by a pressure of 38 atmospheres at 32° F. (0° C.), the gas may be liquefied, the liquid acid having a gravity of 0·83. It may again be noted here, that in liquefying gases by cold and pressure, an *increased pressure* is not necessarily equivalent to a *reduced temperature*, there being a temperature at which a liquefiable gas cannot be liquefied by any attainable pressure. This is termed the "*critical point*," that is, the point where the gas is wavering between the gaseous and the liquid state. Thus, if carbonic anhydride be heated to 88° F. (31·1° C.), a pressure of 109 atmospheres will not effect the liquefaction of carbonic anhydride.

Liquid carbonic anhydride does not mix freely with water, but is soluble in spirit, ether, turpentine, carbonic disulphide, etc. It expands by heat more rapidly than any other known body. Thus at 32° F. (0° C.) it has a specific gravity of 0·947, whilst at 68° F. (20 C.) its sp. gr. is 0·826. If it be cooled to —70° F. (—56° C.), or if it be allowed to escape into the air at ordinary temperatures, it instantly freezes into a snow-white solid, the cold produced by its evaporation in the latter case answering to the artificial cold in the former. It evaporates without melting, inasmuch as the heat it requires for its evaporation keeps it as low as —125° F. (—87·2° C.), whilst it melts at—85° F. (—65° C.). It conducts electricity badly. A cold of —148° F. (—100° C.), is produced by the evaporation of a mixture of solid carbonic anhydride and ether (in which it is soluble) "*in vacuo*."

A heat of 2192° F. (1200° C.) dissociates carbonic anhydride into oxygen and carbonic oxide, re-combination occurring if the mixture be allowed to cool slowly. Similarly, the heat of the electric spark will effect dissociation, the oxygen set free being said to be in an ozonised condition.

At ordinary temperature (15° C.) and pressure (760 mm.), 1 volume of water absorbs 1 volume of the gas ; at 2 pressures, 1 volume of water absorbs 2 volumes ; at 3 pressures, 3 volumes, etc. ; but on the removal of the extra pressure all the dissolved gas escapes except the original volume. Thus, by pressure under the earth, water may be made to take up an extra quantity of gas, whereby the water is rendered effervescent when it comes to the surface. By boiling the whole of the dissolved CO_2 may be driven off.

The rain as it falls dissolves atmospheric carbonic anhydride, the acid rain solution acting on certain rocks, causing their slow crumbling. This process of rock disintegration is moreover assisted by the expansion of the water within the interstices of the rock during congelation. Thus soils are formed of the broken down *débris* ($Na_4SiO_4 + 4H_2O + 4CO_2 = H_4SiO_4 + 4NaHCO_3$). Further, owing to the solubility of the gas in water, the rain conveys it to the roots of plants, the solution dissolving the calcic phosphate which is insoluble in pure water.

(*c.*) *Chemical.*—The volume of CO_2 formed by burning carbon in oxygen, is the same as the oxygen employed. Hence CO_2 contains its own volume of oxygen—in other words the atomic proportion of C:O is as 12:32. Its formula therefore is CO_2, three volumes of the constituent gases being condensed into two volumes. The gaseous, but not the liquid carbonic anhydride, effects a transient reddening of blue litmus. The pure gas instantly extinguishes flame. We may classify the results of dilute carbonic anhydride on flame as follows :—

An atmosphere containing	Action on flame.
16 per cent. of CO_2.	Flame instantly extinguished.
12 ,, ,,	Flame extinguished if not burning vigorously.
10 ,, ,,	Taper burns, but the flame considerably dulled.
8 ,, ,,	Taper burns readily.

Thus it is evident that a taper may burn in a carbonic acid atmosphere that is dangerous and even fatal to animal life.

Potassium burns in carbonic anhydride, setting free carbon ($3CO_2+2K_2=2K_2CO_3+C$). Sodic oxalate is formed when CO_2 is passed into melted sodium ($2CO_2+Na_2=Na_2C_2O_4$), and potassic formate, together with hydric potassic carbonate, when the moist gas is brought into contact with potassium ($2CO_2+K_2+H_2O=KHCO_2+KHCO_3$).

Carbonates are formed by its action on metallic hydrates. (*See* CARBONATES.)

Carbonic acid (H_2CO_3) is not known in a pure state, but seeing that a solution of CO_2 in water reddens litmus, we may assume some such change to occur.

Tests.—A white precipitate with lime or baryta water. Its ready solubility in a solution of potassic hydrate enables us to separate it from most other gases.

COMPOUNDS OF CARBON AND THE HALOIDS.

COMPOUNDS OF CARBON AND CHLORINE.

Carbonic Tetrachloride	CCl_4.
Carbonic Trichloride	C_2Cl_6.
Carbonic Dichloride	C_2Cl_4.
Carbonic Monochloride	C_2Cl_2, or C_6Cl_6.

These compounds are all prepared by indirect methods.

Carbonic Tetrachloride ($CCl_4=154$).

Synonym.—*Bichloride of carbon.*

History.—Discovered by Regnault.

Preparation.—(1.) By the action of chlorine on marsh gas (CH_4). (2.) By passing chlorine and carbon disulphide vapor through a red-hot tube ($CS_2+4Cl_2=CCl_4+2SCl_2$). The sulphur chloride may be separated from the CCl_4 by solution in potassic hydrate.

Properties.—A colorless liquid. Specific gravity, 1·56. Boils at 172° F. (77° C.) ; freezes at —9° F. (—22·8° C.). It is insoluble in water, but is soluble in alcohol and in ether. It freely dissolves fats, resins, etc. Chloroform is formed by the action upon it of zinc and hydrochloric acid. Its vapor is powerfully anæsthetic.

Carbonic Trichloride ($C_2Cl_6=202$).

Synonym.—*Sesquichloride of carbon.*

History.—Discovered by Faraday.

Preparation.—(1.) By the action of sunlight on a mixture of Dutch liquid ($C_2H_4Cl_2$) and chlorine ($C_2H_4Cl_2+4Cl_2=C_2Cl_6+4HCl$).

(2.) By passing the vapor of carbonic tetrachloride (CCl_4) through a red-hot tube.

Properties.—A white crystalline solid, having an aromatic camphory odor. It fuses at 320° F. (160° C.), and boils at 360° F. (182·2° C.), when it sublimes unchanged. It is volatile at ordinary temperatures. It is insoluble in water, but is soluble in ether and in alcohol.

Carbonic Dichloride ($C_2Cl_4=164$).

Synonym.—*Protochloride of carbon.*

History.—Discovered by Faraday.

Preparation.—(1.) By passing the vapors of CCl_4 or of C_2Cl_6 through a red-hot tube.

(2.) By the action of nascent hydrogen on carbonic trichloride (C_2Cl_6).

Properties.—A liquid. Specific gravity, 1·19. Boils at 248° F. (117° C.) It is insoluble in water, but is soluble in alcohol and in ether.

Carbonic Monochloride, C_2Cl_2, or C_6Cl_6.

Synonyms.—*Carbonic subchloride* or *Hexachloride.*

Preparation.—(1.) By passing either the vapor of carbonic dichloride (C_2Cl_4) or of chloroform through a red-hot tube.

(2.) By the action of chlorine on benzene.

Properties.—A white crystalline solid, without odor, insoluble in water, but soluble in ether and in hot alcohol. It melts at 438·8° F., (226° C.), and boils, subliming unchanged, at 627·8° F. (331° C.).

COMPOUNDS OF CARBON WITH BROMINE, ETC.

A *carbonic tetrabromide* (CBr_4) ; a *carbonic tribromide* (C_2Br_6), prepared by the action of bromine on C_2Br_4 ; and a *carbonic dibromide* (C_2Br_4) prepared by acting on ether or alcohol with bromine, all three of which are white crystalline bodies, have been described.

By the action of bromine in sunlight on carbonic dichloride (C_2Cl_4), the crystalline body *carbonic chlorobromide* ($C_2Cl_4Br_2$) is formed.

No compound of Carbon and Iodine has been for certain discovered.

COMPOUNDS OF CARBON WITH OXYGEN AND THE HALOIDS.

Carbonic Oxychloride, $COCl_2$.

Synonyms.—*Chlorocarbonic acid; Carbonyl chloride; Phosgene gas.*

Preparation.—(1.) By exposing equal volumes of carbonic oxide and chlorine to sunlight. The mixture condenses to one-half its original volume.

(2.) By heating together carbonic tetrachloride and zinc oxide ($2CCl_4 + 3ZnO = 3ZnCl_2 + COCl_2 + CO_2$).

(3.) By the oxidation of chloroform.

Properties.—A colorless pungent gas. It is decomposed by water. For this reason it fumes in the air, the chlorine combining with the hydrogen of the moisture ($COCl_2 + H_2O = CO_2 + 2HCl$). By a cold of 5° F. (—15° C.), it may be condensed into a liquid, having a specific gravity of 1·432 at 32° F. (0° C.), and boiling at 46·3° F. (8·2° C.).

With ammonia it forms urea and ammonic chloride :—

$$4NH_3 \quad + \quad COCl_2 \quad = \quad N_2H_4CO \quad + \quad 2NH_4Cl.$$

Ammonia + Phosgene gas = Urea + Ammonic chloride.

This reaction illustrates the property of phosgene gas in effecting the displacement of hydrogen by the substitution of carbonic oxide.

The analogous Bromine and Iodine compounds have not been prepared.

COMPOUNDS OF CARBON WITH SULPHUR AND WITH OXYGEN.

Carbonic Disulphide (CS_2.).

Molecular weight, 76. *Molecular volume*, $\boxed{}\boxed{}$. *Specific gravity*, 1·293. *Fuses at* —148° F. (—100° C.). *Boils at* 110° F. (43·3° C.).

Synonyms.—*Bisulphuret* or *Bisulphide of carbon; Sulphocarbonic acid.*

History.—Discovered accidentally by Lampadius in 1796 whilst distilling iron pyrites.

Preparation.—(1.) By direct union ; viz., by passing the vapor of sulphur over heated charcoal ($C + S_2 = CS_2$). (Some sulphuretted hydrogen may be formed from the hydrogen in the charcoal. The product requires redistillation to free it from dissolved sulphur).

(2.) By heating together charcoal and iron, or charcoal and copper pyrites (Lampadius) ($C + 2FeS_2 = CS_2 + 2FeS$). (Thus CS_2 is formed when coal is distilled, the coal containing iron pyrites).

Properties.—(*a.*) *Sensible.*—An ethereal, colorless liquid, having a peculiar odor, considerably lessened by shaking with mercury.

(β.) *Physiological.*—Its action is anæsthetic, and in excess acts as a poison. It is used for destroying insects in grain.

(γ.) *Physical.*—Specific gravity of liquid, 1·272 ; of vapor, 2·63. It solidifies at —176·8° F. (—116° C.), and boils at 110° F. (43·3° C.). It refracts light powerfully (index of refraction 1·68). It is volatile at ordinary temperatures.

(δ.) *Chemical.*—It has no action on litmus. It fires at 302° F. (150° C.), the products of its combustion being CO_2 and SO_2 ($CS_2+3O_2=CO_2+2SO_2$). It explodes vehemently when mixed with oxygen. It emits a brilliant blue light, of great actinic power when burnt with nitric oxide. Potassium burns in its vapor with the liberation of carbon, and the formation of a potassic sulphide ($CS_2+2K_2=2SK_2+C$). When its vapor is passed over many red-hot metallic oxides, they become changed into sulphides. Passed over heated calcic hydrate (as in some gas-works) CO_2 and H_2S are formed ($CaH_2O_2+CS_2=2CaO+CO_2+2H_2S$). When a mixture of the vapor and sulphuretted hydrogen is passed over hot copper, it yields a sulphide of copper and marsh gas ($CS_2+2H_2S+8Cu=4Cu_2S+CH_4$).

Carbonic disulphide is nearly insoluble in water, but very soluble in alcohol and in ether. It is a solvent, moreover, of many bodies, such as sulphur, phosphorus, iodine, the alkaloids, oils, gums, resins, fats, etc. Hence its use. It is also employed in making thermometers for registering very low temperatures.

It forms one of the most troublesome impurities of coal gas.

Carbonic disulphide combines with alkaline hydrates and with alkaline sulphides to form *sulphocarbonates* ($M''CS_3$) ($6KHO+3CS_2=K_2CS_3+K_2CO_3+3H_2O$). These bodies are analogous to the carbonates, but contain sulphur in the place of oxygen ($CaCO_3$—$CaCS_3$). When the sulphocarbonates are boiled with water they become carbonates. *Sulphocarbonic acid* (H_2CS_3) may be prepared by the action of hydrochloric acid on the salts $(NH_4)_2$ ($CS_3+2HCl=H_2CS_3+2NH_4Cl$). It is a yellow and oily liquid.

Carbonic Oxysulphide (COS).

Molecular weight, 60. *Molecular volume* ☐☐.

This body, which was discovered by Than, may be regarded as H_2S, where $(CO)''$ has replaced the H_2.

Preparation.—(1.) By heating a mixture of sulphur vapor and carbonic oxide.

(2.) By heating together potassic sulphocyanide and dilute sulphuric acid. A hydrosulphocyanic acid is first formed ($KCNS+H_2SO_4=HCNS+KHSO_4$), and afterwards decomposed by the water into carbonic oxysulphide and ammonia, the latter being absorbed by the excess of acid ($HCNS+H_2O=NH_3+COS$).

(3.) By heating a mixture of urea and carbonic disulphide.

Properties.—A combustible, aromatic gas, decomposed by heat into CO and S. It is soluble in water, volume for volume, the solution decomposing spontaneously after a time into carbonic anhydride and sulphuretted hydrogen, the action being immediate if an alkali be present, a sulphide and carbonate of the alkali being formed. It has no action upon an acid solution of lead, copper or silver.

BORON.

Atomic weight, 11. *Molecular weight* (*probable*), 22. *Triad* (BCl_2—BF_3).

History.—Prepared by Davy (1807), by the action of the galvanic current on boracic acid (boric acid). Gay Lussac and Thenard (1808) prepared it by acting on boric anhydride with potassium. Wohler and Deville (1857) first prepared the crystalline modification of boron.

Natural History.—It is never found in nature in a free state. It occurs as boric acid in the lagoons of Tuscany, and in combination with *soda* (borax) as tincal, with *magnesia* as boracite, and with *lime* as boracalcite, etc.

Varieties.—Three varieties have been described, viz., the *amorphous*, the *graphoidal*, and the *crystalline*. The graphoidal modification, however, is probably a compound of AlB_2.

Preparation.—(α.) *Amorphous boron.*

(1.) By fusing together boric oxide and sodium. The residue is then to be acted upon by dilute hydrochloric acid, when the boron remains undissolved ($B_2O_3 + 3Na_2 = 3Na_2O + B_2$).

(2.) By the action of boric oxide, or the vapor of boric chloride, on potassium or on potassic borofluoride ($2BCl_3 + 3K_2 = 6KCl + B_2$).

(β.) *Crystalline* (*diamond or adamantine*) *boron.*

(1.) By fusing boric oxide with aluminium ($B_2O_3 + Al_2 = Al_2O_3 + B_2$). The aluminium must be dissolved out with caustic soda.

(2.) By fusing amorphous boron with silver.

Properties.—The *amorphous* modification of boron is an olive-green powder. It burns in oxygen (forming B_2O_3) and fires spontaneously in chlorine (forming BCl_3). It is insoluble in water. When burnt in air, a trace of boric nitride (BN) is formed, it being one of the few elements between which and nitrogen direct union is possible. It decomposes hot *sulphuric acid* ($3H_2SO_4 + B_2 = B_2O_3 + 3H_2O + 3SO_2$), and cold *nitric acid* ($B_2 + 6HNO_3 = 2H_3BO_3 + 3N_2O_4$). It also decomposes at a red heat the alkaline *carbonates*, *sulphates*, and *nitrates*, setting free carbonic oxide, sulphurous anhydride, and nitric peroxide respectively.

Crystalline, *diamond*, or *adamantine boron*, which, excepting the diamond, is the hardest substance known, has a specific gravity of 2·68, and when pure is colorless, crystalline (octahedral) and a powerful optical refractor. At ordinary temperatures its specific heat is 0·25, but this is doubled at higher temperatures. It mostly contains a trace of aluminium. It is infusible, even in the oxyhydrogen blowpipe, but burns when heated to redness in chlorine. It is not acted upon by strong acids. It forms boric oxide when fused with potassic sulphate ($6KHSO_4+B_2=B_2O_3+3K_2SO_4+3H_2O+3SO_2$), and a borate with the evolution of hydrogen when fused with potassic hydrate ($6KHO+B_2=2K_3BO_3+3H_2$).

Boric (Boracic) **Anhydride** ($B_2O_3=70$; Sp. Gr. 1·83).

Preparation.—By heating boric acid to redness ($2H_3BO_3=B_2O_3+3H_2O$).

Properties.—A clear glass (vitreous boric acid), fusible at a red heat, but not volatile below a white heat. Thus it expels such stronger acids (as sulphuric), which are more volatile, from their salts by heat. (*See* page 6.) It becomes opaque when exposed to the air on account of its hygroscopicity. It is used as a blowpipe reagent, because of its facility for dissolving many of the metallic oxides, forming with them colored glazes.

Boric (Orthoboric or Boracic) **Acid** ($H_3BO_3=62$; Sp. Gr. 1·479).

Preparation and Natural History.—This acid was originally prepared by Homberg (1702) and by Lemery (1727) by the action on borax ($Na_2O,2B_2O_3+10aq.$, called *Sedative Salt,* and when in the rough *Tincal*) either of dilute sulphuric or hydrochloric acid ($Na_2O,2B_2O_3+2HCl+5H_2O=4H_3BO_3+2NaCl$), as suggested by the latter (Lemery), or of dehydrated ferrous sulphate, as suggested by the former (Homberg).

The acid is now obtained as follows :—In certain volcanic districts free and vaporous boric acid is discharged through fissures in the earth accompanied by steam jets (suffioni or fumaroles). We know nothing of its actual origin. For the purpose of condensing these steam jets, brick basins, filled with water from neighbouring springs (lagoons) are erected at the site of the discharge. A series of these lagoons is constructed in a descending line, so that the water may flow from one to the other. The acid solution (containing about 2 per cent. of acid) which collects in the basins, is then evaporated down in leaden pans, the suffioni themselves being employed as the source of heat. The acid is afterwards purified by crystallization.

Properties. (*a.*) *Physical.*—The acid has a bitter taste and crystallizes in scales. At 248° F. (120° C.) it loses water and becomes HBO_2 (*Metaboric acid*), *a tetraboric acid* ($H_2B_4O_7$) being formed at a still higher temperature. Both these acids form unstable salts. At a higher temperature B_2O_3 remains, which at a red heat fuses to a clear glass (*vitreous boric acid*), and at a white heat volatilizes. On boiling the aqueous solution the acid volatilizes with the steam.

It is soluble in 3 parts by weight of boiling water and in 26 parts of cold, but its solubility is irregular. It is soluble in spirit, the solution burning with a green flame.

(β.) *Chemical.*—A solution of boric acid is faintly acid to litmus, but if a piece of turmeric paper be dipped into the solution and dried it becomes of a brown red color. If this be moistened with an alkali it changes to an intense blue.

The acid forms salts called borates, borate of soda ($Na_2B_4O_7$) being a common laboratory re-agent.

Boric Nitride, BN or B_3N_3.

Preparation.—(1.) By heating boron in nitrogen, in air, or in ammonia gas.

(2.) By heating mixtures either of boric oxide and urea, or of borax and ammonic chloride.

Properties.—A white, infusible, and insoluble powder, very stable. It is very slightly acted upon even by boiling acids and alkalies. It is decomposed when fused with potassic hydrate ($BN+3KHO=K_3BO_3+NH_3$) or when heated in a current of steam.

Boric Chloride (BCl_3).

Molecular weight, 117·5. *Molecular volume,* ☐☐. *Specific gravity,* 1·35 *at* 62·6° F. (17° C.). *Boils at* 65° F. (18·3° C.).

Preparation.—(1.) By burning boron in chlorine.

(2.) By passing chlorine over a mixture of red hot boric anhydride and charcoal in a porcelain tube. The BCl_3 must be condensed in a tube surrounded by a freezing mixture :—

$$3Cl_2 + 3C + B_2O_3 = 2BCl_3 + 3CO.$$

Chlorine + Carbon + Boric anhydride = Boric chloride + Carbonic oxide.

Properties.—A colorless, fuming, highly refractive liquid. When acted on with water, hydrochloric and boric acids are formed ($BCl_3+3H_2O=3HCl+H_3BO_3$).

Boric Bromide ($BBr_3=251$).

Specific gravity, 2·69. *Boils at* 194° F. (90° C.).

Its preparation and reactions resemble the chloride.

Boric Fluoride ($BF_3=68$).

Specific gravity, 2·312.

History.—Discovered by Gay Lussac and Thenard (1808).

Preparation.—(1.) By heating in an iron retort a mixture of fluor spar and boric anhydride, and collecting the gas over mercury :—

$$2B_2O_3 + 3CaF_2 = Ca_3B_2O_6 + 2BF_3$$

Boric anhydride + Calcic fluoride = Calcic borate + Boric fluoride.

(2.) By heating a mixture of fluor spar, boric anhydride and sulphuric acid.

Properties.—A colorless, fuming, pungent smelling gas, very soluble in water (700 vols. in 1 of water). Chars paper.

A *fluoboric acid* ($HBO_2.3HF$) and a *hydrofluoboric acid* (HBF_4 or $BF_3.HF$) formed by the action of water on boric fluoride are also known :—

$$\underset{\text{Boric fluoride}}{4BF_3} + \underset{\text{Water}}{3H_2O} = \underset{\text{Hydrofluoboric acid}}{3HBF_4} + \underset{\text{Boric acid.}}{H_3BO_3.}$$

Hydrofluoboric acid forms salts called the borofluorides, such *e.g.* as potassic borofluoride (KBF_4).

These compounds of boron and the haloids combine with gaseous ammonia to form certain molecular compounds such as (BF_3,NH_3).

Boric Sulphide (B_2S_3=118).

Preparation.—(1.) By passing sulphur vapor over heated boron.

(2.) By passing the vapor of bisulphide of carbon over a red hot mixture of boric anhydride and carbon :—

$$\underset{\text{Boric anhydride}}{2B_2O_3} + \underset{\text{Carbon bisulphide}}{3CS_2} + \underset{\text{Carbon}}{3C} = \underset{\text{Boric sulphide}}{2B_2S_3} + \underset{\text{Carbonic oxide.}}{6CO}$$

Properties.—A yellow, fusible, pungent solid. Water decomposes it ($B_2S_3+6H_2O=3H_2S+2H_3BO_3$).

SILICON or SILICIUM (Si=28·2).

History.—Silicon (*silex*, flint) was discovered by Davy (1807), when acting on silicic acid with potassium. Berzelius (1824) obtained it by the action of potassium on fluosilicic acid.

Natural History.—Silicon has never been found in nature in a free state. It occurs (α), in the *mineral* kingdom, as silica (SiO_2), both in a *crystallized* form as quartz, and in a *non-crystallized* form as flint, chalcedony, opal, etc. It also exists abundantly in combination with metallic oxides. Clays are aluminic silicates. (β) In the *vegetable* kingdom it is found in the stems of cereals ; and (γ) in the *animal* kingdom it occurs in teeth, feathers, bone, etc.

Varieties.—Silicon exists in three modifications, viz., (α) an *amorphous* ; (β) a *graphoidal* ; and (γ) a *crystalline* form.

Preparation.—(α.) *Amorphous Silicon.*

(1.) By heating potassium or sodium with potassic silico-fluoride (fluoride of silicon and potassium) :—

$$\underset{\text{Potassic silico-fluoride}}{SiK_2F_6} + \underset{\text{Potassium}}{2K_2} = \underset{\text{Potassic fluoride}}{6KF} + \underset{\text{Silicon.}}{Si.}$$

(2.) By heating sodium in the vapor of silicic chloride ($SiCl_4+2Na_2=Si+4NaCl$).

(β.) *Graphoidal Silicon.* — By fusing together aluminium and amorphous silicon, and afterwards dissolving out the aluminium from the mixture by boiling hydrochloric acid.

(γ.) *Adamantine Silicon.*

(1.) By the fusion of amorphous silicon.

(2.) By heating aluminium in a current of silicic chloride vapor ($3SiCl_4+2Al_2=2Al_2Cl_6+3Si$).

(3.) At high temperatures, silicon dissolves in certain metals, such as zinc, and crystallizes out on cooling. Thus if a mixture of potassic silico-fluoride and sodium be mixed with melted zinc, and the mass covered over with fused sodic chloride and well heated, crystallized silicon may be obtained when the cooled mass is acted upon with acids, which dissolve out all but the silicon.

Properties. — (*a.*) *Amorphous silicon.* A dark brown powder. Specific gravity 2·0. Infusible and non-volatile. It neither conducts heat nor electricity. It burns when heated in air or oxygen, forming SiO_2, or in chlorine, forming $SiCl_4$. It is not acted on by any solvent except hydrofluoric acid (fluorine having a great affinity for silicon), when hydrofluosilicic acid is formed ($Si+6HF=SiH_2F_6+2H_2$). When fused with potassic hydrate, or boiled with a caustic alkali, hydrogen is evolved, and a potassic silicate formed ($Si+4KHO=K_4SiO_4+2H_2$). By fusion with aluminium the graphoidal modification is produced.

(β.) *Graphoidal silicon.* This is found in the form of very hard crystalline metallic-looking scales, having a specific gravity of 2·49. It conducts electricity. It does not burn in oxygen, but fuses at a very high temperature. It is not dissolved by acids generally, nor even by hydrofluoric acid, but is soluble in a mixture of hydrofluoric and nitric acids, hydrofluosilicic acid (H_2SiF_6) being formed. It is slowly acted upon when fused with potassic hydrate.

(γ.) *Adamantine silicon.*—Adamantine silicon is even less prone to oxidation than the graphoidal modification. It resembles crystallized hæmatite both in color and general appearance.

COMPOUNDS OF SILICON AND OXYGEN.

Silica ($SiO_2=60$).

Synonyms.—*Silicon dioxide; Silicic anhydride.*

Natural History.—Silica occurs, in the mineral kingdom, both in a crystalline and in an amorphous form. *Quartz* (*i.e.*, rock crystal, consisting of six-sided crystals terminated by six-sided pyramids), *Amethyst* (the purple color of which is due to iron), *Cairngorm* (a yellow or brown stone), are illustrations of the crystalline variety;

and *Agate*, *Chalcedony* (which in layers of different colors constitutes *Onyx*), *Jasper*, *Cornelian* (the color of which is due to ferric oxide), *Flint* and *Opal* (where the silica is combined with varying quantities of water), are illustrations of the amorphous variety.

Sand is very nearly pure silica. The varying colors of silica depend on the presence of various foreign matters. It forms the chief support of the soil. Plants absorb it freely, as shown by its presence in the stems of rushes and cereals. This, and its presence in solution in certain natural waters, as in the Geysers, prove the possibility of its existing in a soluble form.

All the artificial forms of silica are of the amorphous modification.

Properties.—Pure silica, when *en masse*, is a hard, colorless, transparent body, but when finely powdered has an opaque white appearance. The *crystalline* form has a specific gravity of 2·7, and the amorphous of 2·2. Both forms are non-volatile, but by oxy-hydrogen heat they fuse to a clear glass, the crystalline thereby becoming the amorphous modification. They are insoluble in pure water, and in all acids except hydrofluoric ($SiO_2 + 6HF = H_2SiF_6$ (hydrofluosilicic acid) $+ 2H_2O$). The amorphous form is soluble in solutions of the caustic alkalies, and slightly soluble in solutions of the alkaline carbonates. By heating finely powdered quartz (but not if it be in lump), it is converted into the amorphous variety, and becomes soluble in alkalies.

The ordinary vegetable acids (as *e.g.* tartaric acid), or a weak acid (such as carbonic acid), precipitate silica from its solutions; nevertheless, *at a high temperature*, silica, being non-volatile, decomposes carbonates and even sulphates.

Silica in all its forms when fused with a caustic alkali or alkaline carbonate forms a soluble silicate ($SiO_2 + 2Na_2CO_3 = Na_4SiO_4 + 2CO_2$).

Silica is soluble in fused borax, but not in microcosmic salt.

Silicic Acid.

H_4SiO_4, or $2H_2O,SiO_2$ (*tetrabasic acid*).
H_2SiO_3, or H_2O,SiO_2 (*dibasic acid*).

At the moment that silica is liberated from its soluble compounds, it is soluble in water, silicic acid being thereby formed. This is found in the two modifications mentioned above.

Preparation.—(1.) If silica be fused with sodic carbonate, carbonic acid escapes and a sodic silicate is formed. This salt is alkaline, and soluble in water. If a few drops of hydrochloric acid (*i.e., not sufficient to render it acid*) be added to the solution, it forms a gelatinous mass, from the separation of hydrated silicic acid. If an excess of acid, however, be added (*i.e., sufficient to render it acid*), silicic acid, together with sodic chloride, are produced, and both remain in solution:—

$$Na_4SiO_4 + 4HCl = H_4SiO_4 + 4NaCl.$$
Sodic silicate + Hydrochloric acid = Silicic acid + Sodic chloride.

If this solution be dialysed, the sodic chloride, with any excess of hydrochloric acid, will pass through the dialyser, whilst a pure solution of silicic acid will remain on the dialyser.

Substances that diffuse rapidly (like sodic chloride) are termed *crystalloids*, and those having a low rate of diffusion (such as silicic acid) are termed *colloids.*

(2.) It may also be prepared by the action of carbonic anhydride on a solution of sodic or other soluble silicate. This action is similar to that which occurs in the natural disintegration of granite:—

$$Na_4SiO_4 + 4H_2O + 4CO_2 = H_4SiO_4 + 4NaHCO_3$$
Sodic silicate + Water + Carbonic anhydride = Silicic acid + Sodic carbonate.

(3.) By the action of water on silicic fluoride:—

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6.$$
Silicic fluoride + Water = Silicic acid + Hydrofluosilicic acid.

Properties.—The solution of silicic acid may, by cautious evaporation, be concentrated until it contains 22 per cent. of the acid (H_4SiO_4). In this state it is a colorless tasteless liquid, faintly acid to litmus. By keeping, the acid separates from the water as a gelatinous mass, which shrinks on drying, and when dry has the formula $3(SiO_2),2H_2O$. If this be heated to 212° F. (100° C.), it loses water and becomes $3(SiO_2),H_2O$.

If the solution be evaporated *in vacuo* over sulphuric acid, a lustrous glass is formed, containing 78 per cent. of silicic acid (H_2O,SiO_2). This is insoluble in water, and but very slightly soluble in hydrochloric acid. By further heat the anhydrous acid may be obtained, which is insoluble both in hydrochloric acid and in water, but is soluble in boiling solutions of the caustic alkalies.

COMPOUNDS OF SILICON AND THE HALOIDS, ETC.

Silicic tetrachloride—Tetrabromide—Tetraiodide—Tetrafluoride ... ... $SiCl_4$.–$SiBr_4$.–SiI_4.–$SiFl_4$.
Silicic trichloride ... ... $SiCl_3$.
Silicic hydrotrichloride (Silicon chloroform) $SiHCl_3$.
" hydrotribromide (" bromoform) $SiHBr_3$.
" hydrotriiodide (" iodoform) $SiHI_3$.
(See under hydrogen.)

Silicic Tetrachloride ($SiCl_4$) = 170·2.

Synonym.—*Silicic Chloride.*

Preparation.—(1.) By burning silicon in chlorine.

(2.) By heating carbon and silicic anhydride in a stream of chlorine:—

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

Silicic anhydride + Carbon + Chlorine = Silicon tetrachloride + Carbonic oxide.

Properties.—A transparent, pungent-smelling, colorless, very volatile liquid. It fumes in the air from the deposition of silica by the action of moisture. The specific gravity of the liquid at 32° F. (0° C.), is 1·5237, and of the vapor 5·939. It boils at 138·2° F. (59° C.). Water decomposes it into hydrochloric and silicic acids ($SiCl_4 + 4H_2O = H_4SiO_4 + 4HCl$). By passing the vapor of silicic tetrachloride and sulphuretted hydrogen through a red-hot tube, a liquid having the formula $(SiCl_3)_2\ H_2S_2$ is formed (silicic trichlor-sulphydrate), which on the addition of water is split up into silicic acid, hydrochloric acid and sulphuretted hydrogen.

Silicic Trichloride ($SiCl_3$), formed by acting on silicon heated to 1000° C. with carbon tetrachloride, has been prepared. It is a colorless liquid (sp. gr. 1·58). It fuses at 30·2° F. (—1° C.) and boils at 296·6° F. (147° C.). Its vapor is spontaneously inflammable. Water decomposes it into silicon oxalic acid and hydrochloric acid ($2SiCl_3 + 4H_2O = H_2Si_2O_4$ (Silicon oxalic acid) $+ 6HCl$.)

Several **Silicic oxychlorides** have been prepared.

Compounds of Silicon with Bromine, Iodine, Etc.

Silicic Tetrabromide ($SiBr_4$) is prepared similarly, and has similar reactions to the chlorine compound. It is a colorless, heavy liquid, solidifying at 8·6° F. (—13° C.), boiling at 307·4° F. (153° C.). The liquid has a sp. gr. of 2·813 at 32° F. (0° C.).

Silicic Tribromide (Si_2Br_6) is also a crystalline substance.

Silicic Tetriodide (SiI_4) is a crystalline body, prepared by passing iodine vapor and carbonic anhydride over heated silicon. The CO_2 carries away the SiI_4 as soon as formed, thus preventing decomposition. It is decomposed both by water and by alcohol.

Silicic Triiodide (Si_2I_6) is also a crystalline solid, prepared by the action of metallic silver on SiI_4 ($2SiI_4 + Ag_2 = Si_2I_6 + 2AgI$).

Compounds of Silicon with Fluorine, Etc.

Silicic Fluoride (SiF_4).

Synonym.—*Silicic Tetrafluoride.*

Preparation.—By heating together silica, calcic fluoride and sulphuric acid :—

$$SiO_2 + 2CaF_2 + 2H_2SO_4 = SiF_4 + 2CaSO_4,H_2O.$$

Silica + Calcic fluoride + Sulphuric acid = Silicic fluoride + Dihydric calcic sulphate.

Properties.—A heavy, colorless, fuming gas. Specific gravity, 3·6. It neither burns nor supports combustion. It may be liquefied by

30 atmospheres pressure, or by a cold of −160° F. (—107° C.), and solidified by a cold of —220° F. (—140° C.). By the action of water upon it, silicic and hydrofluosilicic acids are formed, the silicic acid separating as a gelatinous mass, and the hydrofluosilicic acid remaining in solution.

$$\underset{\text{Silicic fluoride}}{3SiF_4} + \underset{\text{Water}}{4H_2O} = \underset{\text{Silicic acid}}{H_4SiO_4} + \underset{\text{Hydrofluosilicic acid.}}{2SiH_2F_6.}$$

Many metallic oxides (as lime) absorb SiF_4 freely.

Silicic Nitride (Formula?) is said to be formed by the direct combination of silica and nitrogen, at a high temperature. It is a white infusible body, soluble only in hydrofluoric acid, forming ammonic silicofluoride. When heated in carbonic anhydride, it forms ammonic carbonate. When heated in steam, ammonia is set free. It is not acted upon by chlorine, nor does heat alone affect it.

Silicic Sulphide (SiS_2) (*bisulphide of silicon*), is prepared either by direct union, or by passing CS_2 vapor over a mixture of charcoal and silica ($SiO_2+CS_2+C=SiS_2+2CO$). It is a white, amorphous, hygroscopic solid, soluble in water, by which it is decomposed into silica and sulphuretted hydrogen ($SiS_2+2H_2O=SiO_2+2H_2S$).

Silico-Formic Acid, or **Leukon** (λευκὸς white) (SiH_2O_2) (*silicon formanhydride*) is formed by the action of water on silicon chloroform ($SiHCl_3$). It is a white substance, decomposed by the caustic alkalies with the evolution of hydrogen. It has a powerful reducing action.

No compound of Carbon and Silicon is known.

CHAPTER X.

HYDROGEN.

Hydrogen:—Compounds of Hydrogen and Oxygen—Water—Compounds of Hydrogen with the Haloids, with Nitrogen, with Phosphorus, with Sulphur and with Selenium—Compounds with Carbon, viz., Methane, Ethylene, and Acetylene—Flame—Compound of Hydrogen and Silicon.

HYDROGEN (H = 1).

Atomic weight, 1. *Monad, as in* HCl. *Molecular weight,* 2. *Molecular volume,* ☐☐. *Relative weight,* 1. *Specific gravity,* 0·0693 100 *cubic inches weigh* 2·1430 *grains at* 60° *F. and* 30 *B.P. and* 1 *litre* = 1 *crith, i.e., weighs* 0·089578 *grm.* 1 *grm. at* 0° *C. and at* 760 *mm. pressure measures* 11·19 *litres, and* 1 *grain at* 60° *F. and* 30 *B.P. measures* 46·729 *cubic inches.*

Synonyms.—*Inflammable Air or Gas* (Cavendish, 1781; *Phlogiston* (older chemists); *Hydrogen* (ὑδωρ water, and γενναω I produce) (Associated French Chemists).

History.—The alchymists described "an inflammable air," which was, no doubt, hydrogen. It was studied by Paracelsus in the sixteenth, and by Hales in the seventeenth century, when engaged in examining the gas produced by the distillation of coal. Cavendish (1766) examined it more carefully, and was the first to set it free by the action of acids on metals. Its properties were afterwards investigated by Watt, Priestley, Volta, and others.

Natural History.—(*a.*) *In the mineral kingdom* it is found free in volcanic gases (to the extent, at times, of 25 per cent.), also in the gases given off from the oil-wells of Pennsylvania, in firedamp, and occluded in meteorites (Graham and Mallet; Dewar). (*See* page 231.) It is also assumed from spectroscopic observation to be present in the atmosphere of the sun, certain stars, etc., the temperature being too great to allow of union existing between hydrogen and other elements. In a combined state, it forms one-ninth part by weight of water, three-seventeenths of ammonia, one-seventeenth of sulphuretted hydrogen, etc. Along with chlorine it is found in certain mineral springs. (*β.*) *In the vegetable kingdom* it is found as a constituent of all tissues, as well as in the water with which in all cases the tissue is associated;

whilst (γ), *In the animal kingdom* it is always found in the tissues, and occasionally in a free state in the breath and in intestinal gases from the spontaneous decomposition of animal and vegetable matters.

Preparation.—(1.) By the electrolysis of acidulated water, the hydrogen being set free at the negative pole.

(2.) By the action of an intense heat on water.

(3.) By the action of sodium or potassium, or an amalgam of sodium or potassium on water at common temperatures :—

$$2H_2O + Na_2 = 2NaHO + H_2.$$

Water + Sodium = Sodic hydrate + Hydrogen.

[NOTE.—With potassium the heat evolved by the union of the oxygen and potassium is sufficient to fire the hydrogen, but this does not occur in the case of sodium unless the water be hot.]

(4.) By passing steam over certain red hot metals, such as iron, or by subjecting steam to an intense heat, such as that of the electric arc :—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

Iron + Water = Black or magnetic oxide of iron + Hydrogen.

[NOTE.—Metallic platinum cannot be made to decompose water except at a very high temperature, but if the platinum be intimately associated with magnesium or with zinc, decomposition of the water may be effected at ordinary temperatures. Copper decomposes water at a very high temperature, but if the copper be associated with zinc it then decomposes it at ordinary temperatures. (Proceedings of R. S., 1872, pp. 133, 218.)]

(5.) By the action of heated sodium on gaseous hydrochloric acid :—

$$2Na + 2HCl = 2NaCl + H_2.$$

Sodium + Hydrochloric acid = Sodic chloride + Hydrogen.

(6.) By the action of heat on formates (or oxalates, etc.), in the presence of an excess of an alkali :—

$$KCHO_2 + KHO = K_2CO_3 + H_2$$

Potassic formate + Potassic hydrate = Potassic carbonate Hydrogen.

(7.) By passing steam over red hot coke or charcoal (Deville and Debray) :—

$$2H_2O + C = 2H_2 + CO_2.$$

Water + Carbon = Hydrogen + Carbonic anhydride.

[NOTE.—The CO_2 may be removed by lime. If the heat be very great, CO (and not CO_2) is formed, which is not capable of removal by lime].

(8.) By the action of hydrochloric or dilute sulphuric acid on zinc, magnesium, iron, and certain other metals :—

(α.) $Zn + 2HCl = ZnCl_2 + H_2.$

Zinc + Hydrochloric acid = Zincic chloride + Hydrogen.

(β.) $Fe + H_2SO_4 = FeSO_4 + H_2.$

Iron + Sulphuric acid = Iron sulphate + Hydrogen.

[NOTE.—(α.) On closing the vessel in which hydrogen is generated by the action of dilute sulphuric acid on zinc, the pressure of the gas stops further decomposition. It has been suggested that, in this case, pressure stops affinity by preventing the escape of bubbles of hydrogen, the effect of which ordinarily is to displace the zincic sulphate solution immediately surrounding the zinc. This being stopped, fresh acid is prevented from coming into contact with the metal. (β.) The hydrogen prepared by the action of acids on metals is not pure, but may contain *certain compounds of hydrogen and carbon,* the carbon being derived from carbon in the iron if it be used for the purpose (which may be removed by passing the gas through wood charcoal), or *sulphuretted hydrogen* (removed by passing the gas over glass beads moistened with a solution of lead nitrate or caustic potash), *arseniuretted and phosphoretted hydrogen* (absorbed by an aqueous solution of silver sulphate), *traces of oxygen* (removed by passing the gas through a red-hot iron tube), *moisture* (absorbed by phosphorus pentoxide), etc.]

(9.) By the action on zinc or aluminium of a solution of potassic hydrate :—

$$2KHO + Zn = ZnK_2O_2 + H_2.$$

Potassic hydrate + Zinc = Potassic zincic oxide + Hydrogen.

(10.) By immersing zinc placed in contact with iron in a solution of an ammoniacal salt (excepting a solution of ammonic nitrate), heated to 104° F. (40° C.), the action being assisted by the presence of free ammonia (Lorin).

(11.) By submitting certain organic substances to destructive distillation. Thus it is found in coal-gas along with hydrocarbon vapors and other organic compounds.

Properties.—(α.) *Sensible.*—When pure, hydrogen is a colorless gas, without taste or odor.

(β.) *Physiological.*—Hydrogen is not a poison. Thus it may be breathed for a few seconds (when pure) with impunity, the voice being rendered peculiarly shrill under its influence. If breathed continuously, death results from want of oxygen, but not from direct toxic effects of hydrogen.

(γ.) *Physical.*—Hydrogen is the lightest body known, being 14·435 times lighter than air (sp. gr. 0·0693). At Paris latitude, at 0° C. and at a pressure of 760 mm. of mercury, one litre weighs 0·089578 grm. (1 litre of air weighing 1·293 grm., and 1 litre of oxygen 1·429 grm.), or 1 grm. occupies 11·1636 litres. (Regnault.) Thus hydrogen is employed for balloons. Sound travels with three times greater rapidity in it than in air. It refracts light more powerfully than any other gas (1·000138), its power in this respect being six times as great as air at the same temperature and density. Up to a certain pressure hydrogen obeys the law of Boyle (p. 39), but at very high pressures certain exceptional results are recorded. Thus at 1015 atmospheres it is only reduced $\frac{1}{628}$th of its volume.

Hydrogen has been liquefied by Pictet, and also by Cailletet (1877), by the combined action of extreme cold —220° F. (—140° C.) and pressure (650 atmospheres). By Cailletet's arrangement, after a pressure of 300 atmospheres has been effected, the tube upon a reduction of pressure becomes filled with a kind of fog, showing the gas to have been condensed to minute particles of liquid. By Pictet's arrangement a cold of —210° F. (—140° C.) is obtained by the vaporization of liquid sulphurous and carbonic acids. The hydrogen thus liquefied is said to solidify by the rapidity of its own evaporation so soon as the liquid hydrogen is allowed to escape.

Hydrogen exhibits in a remarkable degree the power of *diffusion*, *i.e.* a power due to the constant motion and mutual repulsion of gas particles. If a bottle of hydrogen be connected vertically by a glass tube with a bottle of oxygen, the oxygen (the heavier gas) being below, the hydrogen, against the action of gravity, will descend, and the oxygen ascend, a complete intermixture of the gases resulting. Similarly, if a vessel be divided into two parts by a porous diaphragm or a thin plate of artificial graphite, one-half being filled with one gas and the other half with another gas, diffusion will take place until the admixture of the gases is complete. But the rate of diffusion is not alike. Graham's law is expressed thus :—"*The diffusibility of two gases varies inversely as the square roots of their densities.*" Thus, the density of $H = 1$ and of $O = 16$, therefore the diffusibility of these two gases is as 4 to 1 ; in other words, the diffusion of four cubic inches of hydrogen will occupy the same time as the diffusion of one cubic inch of oxygen.

The "*diffusiometer*" of Graham is a glass tube, closed at one end by some porous material, such as well-dried plaster of Paris. If this be filled with hydrogen, and the open end placed in water, the water rises rapidly in the tube, because the hydrogen passes through the porous diaphragm (*i.e.*, diffuses) at a greater rate than the air enters ; *i.e.*, $H = 1$, and air $= 14{\cdot}47$, therefore their relative diffusibility $= \sqrt{14{\cdot}47}$ to $\sqrt{1}$, or as 3·8 to 1 ; or, for every 1 cubic inch of air entering the tube, 3·8 cubic inches of hydrogen escape. It will be seen, therefore, that by this means a mixture of two gases of unequal diffusibility may be partially separated (*atmolysis*).

It will be evident that diffusion becomes an important agent by which to determine whether a gas is homogeneous or a mixture of gases. Supposing a gas of known composition (a compound of C and H) be placed in a diffusiometer, and the residue in the diffusiometer be found to contain C and H in the same proportion as the original gas, chemical homogeneity may be assumed, and *vice versâ*. Still it must be noted that if a mixture of two gases be present in the ratio of their coefficients of diffusion, the composition of the residue after diffusion would be the same as before diffusion. An error from this cause might result, a compound gas being assumed to be homogeneous.

By the term *osmosis*, we imply not simply diffusion through small apertures, but the passage through membranous diaphragms. Here, adhesion between the membrane and the gas plays its part in the process, as well as diffusion.

Occlusion.—We have remarked that hydrogen is found *occluded*, that is, absorbed, in meteoric iron. (Dewar.) (Proc. R. S., XV. 502.) If hydrogen be passed over a red-hot plate of iron, the iron will absorb 0·46 times its volume. The meteoric iron of Lenarto yields 2·85 its volume of a gas containing 85·68 per cent. of hydrogen. Probably, therefore, this iron has been exposed to hydrogen at greater pressure than the earth pressure. Platinum at 100° C. absorbs 0·76 volume, and at a red heat 3·8 times its volume of hydrogen. Palladium absorbs 376 volumes at common temperatures, 643 volumes at 194° F. (90° C.), and 526 volumes at 473° F. (245° C.). Electrolytically deposited palladium heated in hydrogen to 212° F. (100° C.) will absorb 982 volumes. The metal after the occlusion of the hydrogen, although not altered in appearance, has a diminished tenacity, its specific gravity and conducting power for heat and electricity being also reduced. The occluded hydrogen is in every case completely evolved on the application of heat, the absorbed gas possessing more than ordinary chemical activity. For if the palladium containing the occluded hydrogen be placed in a jar of chlorine, or in an iodine solution, hydrochloric and hydriodic acids will be formed, whilst, by similar means, ferric oxide may be changed to ferrous oxide. Graham held that in this and like cases (though of this there is considerable doubt), an alloy of palladium (probably Pd_2H) or of other metal and hydrogen was formed. To the hydrogen, in this state of supposed combination, he gave the name "*hydrogenium*," in order to denote a kind of solid, quasi-metallic nature). Dewar and others have estimated, but variously stated, its specific gravity in this condition, as 0·863, 0·733, and 0·620, this last number being equal to the condensation of seven litres of gas into one cub. c. (Dewar.) Hydrogenium is stated to be magnetic, and to have an electric conductivity of 5·99 (Pd being 8·1 and Cu 100).

The analogy between hydrogen and the metals is well marked, nor is the fact of its gaseous condition any argument against its metallic nature. The hydrogen spectrum consists of four bright lines, one each in the blue and indigo, and one corresponding to the C and F lines respectively.

Hydrogen dissolves in water, or more accurately in the proportion of 0·0193 volume, at 0° C. and 760 mm. [*coefficient of absorption*] in one volume of water at similar temperature and pressure to the extent of $\frac{1}{50}$th of its volume. Unlike most gases, however, it is equally soluble at all temperatures from 0° to 20° C. Alcohol dissolves a greater volume of the gas than water, but its solubility in alcohol decreases with increase of temperature.

(*c.*) *Chemical.*—Hydrogen has no action on litmus or turmeric. It will not support combustion, but it burns, when pure, with a perfectly non-luminous and enormously hot flame, any light emitted being due to some impurity, such as a trace of sulphur either in the air or in the gas. Water is the only product of its combustion (noted by Macquer, 1766). In burning, it produces a greater heat than an equal bulk of any known substance, one gramme of hydrogen, in combining with eight grammes of oxygen, produces sufficient heat to raise 34,462 grammes of water 1° C. [= 62,031 grains 1° F.] The calorific power of hydrogen, therefore, is equal, we say, to 34,462 *thermal units.*

With *oxygen*, hydrogen does not combine under ordinary circumstances ; but by heat, or by the action of spongy platinum, or if the gases be nascent, combination may be easily effected. This combination of oxygen and hydrogen occurs with considerable violence, an explosion resulting from the sudden expansion caused by the heat developed by the combination.

In the case of the *haloids,* heat is required to effect the chemical union of hydrogen with iodine and fluorine, whilst daylight is sufficient to effect its combination with chlorine and bromine.

With *nitrogen*, combination may be effected directly, if the gas be in a nascent state, when ammonia is formed.

With *carbon* and *sulphur*, the direct union, and with *phosphorus, selenium, silicon,* etc., the indirect union of hydrogen may be effected.

With *antimony* and *arsenic,* hydrogen, when nascent, forms gaseous combinations.

The *acids* have no action upon it, except that nascent hydrogen reduces nitric acid.

The *alkalies* are also without action upon it.

With the *metals*, hydrogen forms but few compounds.

Metallic oxides are unaffected by hydrogen, unless they be red-hot, when they are reduced.

It decomposes at a high temperature, certain *metallic sulphides and chlorides,* setting free the metal, sulphuretted hydrogen or hydrochloric acid being formed.

Comparing hydrogen with oxygen, we may note their remarkable chemical dissimilarity. Thus oxygen combines with all the elements except fluorine, and, as a rule, directly, whereas the hydrogen compound with fluorine is easily formed, and is of great stability ; moreover, hydrogen combines directly with none of the elements except with oxygen, carbon, sulphur, and the haloids fluorine excepted. The combining power between oxygen and the metals is intense, whilst that between hydrogen and the metals is almost *nil.*

Its proportion in gaseous mixtures may be determined by a eudiometric experiment, as already described (page 98).

COMPOUNDS OF HYDROGEN AND OXYGEN.

Water ... ... H_2O.
Peroxide of hydrogen ... ... H_2O_2.

WATER (H_2O).

Molecular weight, 18 ; *Density*, 9 ; *Specific gravity*, 1·000.

History.—Water was regarded by the ancients as an element. Thales (600 B.C.) describes it as the origin of all things ; Van Helmont (1600 A.D.) estimated the quantities present in various animal, vegetable, and mineral compounds. Priestley (1780) correctly predicted its composition, from noting the moisture formed on firing a mixture of air and hydrogen. Watt and Cavendish (1781-1783) confirmed Priestley's predictions by more accurate experiments, proving its compound nature and the proportions of its constituents. Lavoisier and Laplace (1783-4) added further confirmatory proofs of its exact composition.

Natural History.—(*a.*) In the *mineral* kingdom it is found in the atmosphere as clouds and mist, also as rain, snow, and hail ; (*b*) in seas and rivers. It also occurs (*c*) below the surface of the earth to a certain depth, thrown up here and there as springs, and (*d*) lastly, combined in many minerals as hydrates, as water or the elements of water uncombined (zeolites). (*β.*) A large percentage of *vegetable* and *animal* matter is water.

Preparation.—Chemically pure water is not found in nature. It may be prepared by *distillation*, that is, by vaporizing the water and condensing the vapor.

Composition:—

			By volumes.	By weight (atomic).	By weight (percentage).
Hydrogen	H_2	=	2	2	11·11
Oxygen	O	=	1	16	88·89
	H_2O	=	3	18	100·00

The two volumes of hydrogen combining with one volume of oxygen become condensed into two volumes of water gas.

Proofs of its composition.—These are both analytical and synthetical:—

(A.) *Analytical.* (1.) By the electrolysis of water.

Placing the platinum terminals of a galvanic battery in a weak acid solution, the acid being added to increase the conductivity of the water, hydrogen will be immediately evolved from the negative pole, and oxygen from the positive. The volume of oxygen so evolved is *slightly less* than one-half the volume of hydrogen. It should be exactly one-half, but (1) oxygen is more soluble than hydrogen in water, and (2) some of the oxygen evolved is in an ozonized condition (proved by its action on iodized starch water), in which form three volumes are condensed into two. Experiment proves that water is made up of 2 *volumes of hydrogen* in chemical combination with 1 *volume of oxygen.* The same fact might also be demonstrated by passing sparks from the induction coil through steam (whereby it is decomposed), and analyzing the products formed.

Oxygen is sixteen times heavier than hydrogen. The bulk of hydrogen in water being twice that of the oxygen, it follows, that in 18 parts by weight of water we have 2 *parts by weight of hydrogen* + 16 *parts by weight of oxygen.*

(2.) That water is made up of oxygen and hydrogen in these proportions by weight may be proved by passing steam over a weighed quantity of red-hot iron, whereby the water is decomposed, hydrogen being set free, and an oxide of iron formed. The hydrogen may be measured and its weight estimated, whilst the weight of the oxygen in combination with the iron may also be determined.

(B.) *Synthetical.* (1.) If two volumes of hydrogen and one volume of oxygen be fired in a eudiometer by an electric spark, they combine with explosion, the explosion resulting from the energetic and rapid combination, attended with sudden expansion and great evolution of heat. It is necessary that the eudiometer should be surrounded by a wider tube, through which steam is passed, in order to maintain the product in the state of vapor. The water gas (H_2O) formed will measure, under identical conditions of pressure and temperature, two-thirds the bulk of the original gases, or, in other words, three volumes of the mixed gases will be found to form two volumes of steam. (Cavendish.) (*See* page 34.)

It may further be noted that combination in these proportions is constant. If oxygen and hydrogen be mixed in arbitrary proportions and exploded, combination always occurs in the proportion of two volumes of hydrogen to one volume of oxygen, whilst the gas added in excess remains unaltered after explosion.

(2.) If a stream of pure hydrogen be passed over a weighed quantity of hot and well-dried cupric oxide, the hydrogen will deprive the copper of its oxygen, and steam be formed. If the water be collected and weighed, and the weight of the reduced copper be also estimated (the loss being oxygen, ascertained), we shall be able to determine the relative weights of oxygen and hydrogen present in the water so formed. (Dulong and Berzelius, Dumas and Boussingault.)

(3.) Water is the only product of the combustion of hydrogen in air or oxygen. And, moreover, whenever combustible bodies containing hydrogen, (such as tallow, oil, coal gas, etc.,) burn with flame, water is always found as one product of combustion.

It may here be noted that enormous heat is evolved by the union of hydrogen and oxygen. Thus, the oxy-hydrogen jet supplies us with a heat almost unsurpassed by chemical means.

Properties.—(α.) *Sensible.*—Water (when pure) is usually said to have neither color, taste, nor smell. As regards its *color*, we note that when a layer of six feet is examined by transmitted light, it appears of a blue tint, and in still greater bulk, as seen in the Swiss lakes, of a bluish green tint. The presence of organic matter, however, even in minute quantity, imparts a brownish tinge to the water, so much so, that the tint-depth may be taken as a rough indication of the amount of organic matter present in solution.

As regards its *odor*, although this cannot be detected by man, animals smell it at long distances, as shown in the case of horses and camels in the desert.

Physical.—(β.) The specific gravity of water at 39·2° F. (4° C.), (its point of maximum density) is regarded as 1·000, and has been adopted as the standard of comparison for solids and liquids.

Water may exist in the *solid, liquid* or *gaseous* state. The change from the solid into the liquid, or from the liquid into the gaseous state, involves the absorption of heat.

As to its *weight*—

1 cub. in.	of water	weighs	(62° F. or 16·7° C.)	252·456 grs., Sp. Gr. 1·000
,,	of ice	,,	(32° F. or 0° C.)	235·000 grs., Sp. Gr. 0·91674
,,	of steam	,,	(212° F. or 100° C.)	0·1932 gr., Sp. Gr. 0·623 (0·0693×9)

Water is therefore about 825 times heavier than air. A *cubic foot* weighs about 1000 ozs. avoird. (actually 997 ozs.) ; *one gallon*, 70,000 grains, or about 10 lbs. avoird. [*]; 1 *litre* (at 4° C.), 1000 grammes, or 1 kilogramme.

Water is practically incompressible. Every atmosphere contracts it about fifty-one-millionths of its bulk; in other words, a pressure of 30,000 lbs. will force 14 volumes into 13. (Regnault.)

The action of heat.—At all temperatures, water evaporates. At 32° F. (0° C.) it freezes (hexagonal system). If this frozen water be heated it melts, but until the whole of the ice be melted the liquid remains at 32° F. (0° C.), notwithstanding the application of heat. After the ice is melted, its temperature gradually rises as the heat is continued up to 212° F. (100° C.), when the water boils (*i.e.* at 760 mm. pressure), whilst if the heat be applied long enough, the water entirely boils away.

I.—We say, then, water freezes or becomes solid at 32° F. or 0° C. But the exact temperature of freezing is influenced by a variety of circumstances. The *melting point of ice* is more constant than the *freezing point of water* ; hence, the former is usually employed in graduating thermometers. The circumstances influencing the temperature of freezing are as follows :—

[*] "A pint of water
Weighs a pound and a quarter."

(α.) The presence of atmospheric air. In closed vessels, at perfect rest and *out of contact with air*, the temperature of water may be lowered to 14° F. (—10° C.) without solidification, but if the water at this temperature be shaken, it instantly freezes, the temperature immediately rising to 32° F. (0° C.).

(β.) In closed vessels, *air being present*, or in very narrow tubes, water may be cooled to 5° F. (—15° C.) without freezing, solidification occurring on the slightest motion being imparted to the liquid.

(γ.) If water be surrounded by certain mixtures (such as chloroform and sweet almond oil, which may be mixed in such proportions that the liquid has the same density as water), the water thus encircled may be cooled, without solidifying, to —4° F. (—20° C.). If, in this state, however, it be touched with a piece of ice, it instantly freezes and expands.

(δ.) Pressure.—The melting point is lowered 0·0075° C. for every additional atmosphere. At a pressure, therefore, of 13,000 atmospheres, ice would be converted into water at 0·4° F. (—18° C.). Water at 39·2° F. (4° C.), enclosed in a perfectly tight vessel where expansion is impossible, will not freeze although cooled below zero. The ice crystals are rhombohedric and six-sided prisms.

II. On heating ice at 32° F. (0° C.), we note that the application of heat does not raise the temperature until the whole of the ice is melted. Thus, *ice* at 32° F. (0° C.) *uses up* heat to become *water* at 32° F. (0° C.). The amount of heat thus used up by a given amount of *ice* is called *the latent heat of water*, in other words the latent heat of fusion of ice. It is latent in the sense that it does not affect the thermometer, but effects a difference in the condition of the molecules in their relationship to each other. In passing from the solid to the liquid state this latent heat is re-evolved. A pound of *water* at 32° F. (0° C.) mixed with a pound of water at 175° F. (79·44° C.) will have a mean temperature of $\frac{32 + 175}{2} = 103{\cdot}5°$ F., whilst a pound of *ice* at 32° F. (0° C.), mixed with a pound of water at 175° F. (79·44° C.) will have a temperature of 32° F., *but the ice will have melted*, 143 degrees F. having been required for this purpose. Note, therefore,

$$175 - 143 = 32\text{; temperature of liquid} = \frac{32 + 32}{2} = 32°\text{ F.}$$

We regard, therefore, 143° F. (79·4° C.) *as the latent heat of water*; in other words, 143° F. (79·4° C.) is the heat, unrecognisable by a thermometer, absorbed by 1 lb. of ice in becoming water. In other words one gram of ice at 0° C. is converted into one gram of water at 0° C. by the disappearance of 79·4 thermal units.

Water has the highest latent heat of known liquids.

[For explanation of thermal unit, or unit of heat, *vide* page 45.]

III.—Ice presents a peculiar phenomenon termed "*Regelation.*" Two pieces of ice, on being squeezed together, cohere. This cohesion ("regelation") is probably due to a certain portion of the ice becoming melted at the points of contact, owing to a lowering of the melting point by pressure. Instantly, however, that the pressure is removed, the water solidifies.

IV.—After a sufficiency of heat has been applied, the water boils. Water evaporates spontaneously (that is, gives off vapor) at all temperatures. Spontaneous evaporation implies certain molecules finding their way into the space above the liquid, which space if limited will ultimately become "saturated," *i.e.*, when the molecules given off from the surface are numerically the same as the molecules that fall back into the liquid. The vapor thus given off by a liquid has a certain "elastic power," or "*tension.*" Air also has an "elastic power," or "tension," capable of supporting 760 mm., or nearly 30 inches of mercury; in other words, air has an elastic power capable of exerting a pressure of 15 lbs. on every square inch. When the tension or pressure of the vapor given off by a liquid under the action of heat, balances the tension or pressure of the atmosphere, the liquid is said to boil. This in the case of water occurs at 212° F. (100° C.).

V.—Various circumstances influence the temperature at which water boils:—

(*a.*) Boiling, we have said, is the "temperature at which the pressure or the tension of the evolved vapor balances the pressure of the atmosphere." Hence, by lessening the pressure the boiling point of a liquid may be lowered, and *vice versâ.* But for every liquid there is a temperature at and beyond which pressure is ineffectual to restrain the liquid passing into the gaseous condition. This is termed "*The critical point.*" Thus if some liquid CO_2 be confined in a strong glass tube over which a little warm water be poured, a point will arrive when the whole of the liquid suddenly disappears. Probably the critical point is when vapor and liquid have the same specific gravity. (Ramsay.) The facts relating to the phenomena of the critical point indicate the impossibility of liquefying certain gases at ordinary temperatures by pressure only. Hence, in the liquefaction experiments of Pictet and others, where oxygen, hydrogen, nitrogen, carbonic oxide, etc., have yielded, these experimenters have combined intense cold with great pressure. Inasmuch as the pressure of the atmosphere constantly varies, it follows that the boiling-point of water must be constantly varying. It is only when the barometer is at 760 mm. (that is, the mean height of the barometer at the sea-level) that water boils at 100° C., the boiling-point being reduced 1° C. for every 27 mm. that the barometer falls. If water be placed under the exhausted receiver of an air-pump it may be made to boil even at common temperatures. On Mont Blanc (417 mm. pressure), water boils at 183·2° F. (84° C.). It will be seen, therefore, that by noting the temperature at which water boils, by means of what are called *hypsometric thermometers,* we may infer, approximately, the elevation. For every 590 feet the boiling point is lowered about 1 degree F., or 1 degree C. for every 1,062 feet.

The following table gives the tension of aqueous vapor at different temperatures. It will be noted that at 212° F. (100° C.), the vapor tension of water is equal to the pressure of the atmosphere (760 mm.). Hence water boils at 212° F., or 100° C. :—

Tension of the vapor of water (Regnault).

Temperature.		Tension in Mm. of Mercury.	Temperature.		Tension in Mm. of Mercury.
°F.	°C.		°F.	°C.	
— 4	— 20	0·927	104	40	54·906
+ 14	— 10	2·093	122	50	91·982
32	0	4·600	140	60	148·791
41	+ 5	6·534	158	70	233·093
50	10	9·165	176	80	354·280
59	15	12·699	194	90	525·450
68	20	17·391	212	100	760·000
86	30	31·548			

The above diagram will show the importance when graduating thermometers, of accurately noting the barometric pressure at the time of graduation.

Further by *increasing* the atmospheric pressure the temperature at which water boils will also be increased. With one atmosphere (*i.e.*, 760 mm. pressure) we have seen that water boils at 212° F. (100° C.); with two atmospheres it requires a heat of 249° F. (120·6° C.) ; with three atmospheres, of 273° F. (133·9° C.) ; with ten atmospheres, of 356·5° F. (180·3° C.); with twenty atmospheres, of 415·4° F. (213° C.); and so on.

(*β*.) The boiling point varies with the purity of the liquid, as for example, the presence of solids in solution, increasing with the degree of concentration, the adhesion of solids to liquids being greater than the cohesion between the molecules themselves. Thus in the case of water :—

A saturated solution of sodic carbonate boils at 104·6° C. or 220·2° F.
,, ,, ,, sodic chloride ,, 108·4° C. or 227·0° F.
,, ,, ,, potassic nitrate ,, 115·9° C. or 240·6° F.
,, ,, ,, sodic nitrate ,, 121·0° C. or 249·8° F.
,, ,, ,, potassic carbonate ,, 133·0° C. or 271·4° F.
,, ,, ,, calcic chloride ,, 179·5° C. or 355·1° F.

(*γ*.) The boiling point depends on the depth of the bulk heated. A column 32 feet deep would not *completely* boil—that is, give off vapor from the bottom of the vessel—at a lower temperature than 249·8° F. (121° C.).

(*δ*.) The boiling point varies with the vessel in which the water is boiled. The adhesion of water for glass is greater than the adhesion of water for metal. This adhesion must be overcome; and hence, in the case of very clean glass, the adhesion between the glass and the water particles may raise the boiling point 1 or 2 degrees. Hence to determine boiling points accurately, the temperature of the vapor and not of the liquid should be recorded.

By the term "*superheated*" is implied the raising the temperature above the boiling point without ebullition.

(ε.) In boiling, the cohesion of the particles of water for one another has also to be overcome by heat. The presence of gases in solution lowers the boiling point by destroying this attraction of the water particles, and, conversely, the absence of dissolved gases heightens the boiling point.

VI.—The *latent heat of vapors* is the heat that disappears in the change from a liquid to a gas. This latent heat is evolved in the opposite molecular change from the gas to the liquid. *The latent heat of steam* is said to be 997 degrees F., or 537 degrees C. (*i.e.*, 537 thermal units); (*i.e.*) 1 gram of steam will raise 537 grams of water through 1 degree C. Or putting the facts in a more practical form, the heat required to boil away 1 lb. of water at 212° F. (100° C.) will raise 5·37 lbs. of water from 32° to 212° F. (=180 degrees F.), [or from 0° to 100° C. (=100 degrees C.)]; or if the steam from 1 lb. of water be conveyed into 5·37 lbs. of water at 32° F. (0° C.), it will raise it to 212° F. (100° C.).

$$(180 \times 5{\cdot}37 = 996{\cdot}66, \text{ or } 100 \times 5{\cdot}37 = 537).$$

VII.—If a drop of water be placed on a red-hot platinum dish, it assumes what is called *the spheroidal condition;* that is, the spheroid rests on a cushion of its own vapor, which, being a bad conductor of heat, prevents the spheroid of water boiling. The temperature of the spheroid has been ascertained to be about 194° F. (90° C.), whilst the space between the spheroid and the dish is said to be about 0·15 to 0·25 mm.

VIII.—On subjecting water to the action of cold, it gradually contracts until it reaches a temperature of 39·2° F. (4° C.). This temperature is what is called "*the maximum density of water*," *i.e.*, distilled water. [We should note that the presence of soluble salts lowers the maximum density, so that in sea-water it is below 32° F. (0° C.)] At this point of maximum density a given bulk of water weighs more than at any other temperature. Hence 1c.c. of water, at 39·2° F., or 4° C., is taken as representing a gramme weight. Below 39·2° F. (4° C.) water expands rapidly, so that ice floats on water, owing to its less specific gravity. The sp. gr. of water at 0° C. is 0·99987, whilst that of ice at 0° C. is 0·91662. (1 volume of water at 0° C. becomes 1·09082 volume of ice). Thus water-pipes break, rocks disintegrate, and rivers and lakes freeze only on the surface, the ice easily melting as the warm weather returns. At 39·2° F. (4° C.) convection in (*i.e.*, the circulation of) rivers and lakes ceases.

When water is heated from 39·2° F. (4° C.) it expands; 1 volume of water at 39·2° F. (4° C.), becoming 1·04312 volumes at 212° F. (100° C.).

We may here note that aqueous vapour is very opaque to heat. Thus the moisture of the air prevents radiation from the earth.

Water is a simple refractor of light, its refracting power increasing as it is cooled. This increase of refraction is not interfered with by its expansion below 39·2° F. (4° C.). (Arago and Fresnel.)

Water as a neutral solvent is unsurpassed. Solution is generally a purely *physical* act, neither heat nor change of property resulting. The act of liquefaction (*i.e.*, the passage from a solid to a liquid) is usually accompanied by cold (*i.e.*, the absorption of heat).

I. *Solubility of solids.*—The *rapidity* with which a solid dissolves depends—(1) on whether the solid be in lump, or finely powdered; and (2) on the motion imparted to the mixture. In the *first* case, powdering the body increases the surface upon which the water acts; and in the *second*, motion removes the saturated solution surrounding the solid, thus bringing fresh and unsaturated portions of the solvent into contact with the material. If such motion be not imparted to the menstruum during the period of action, solution is slow and only proceeds by "*liquid diffusion*" (a process analogous to "*gaseous diffusion*"), *i.e.*, *the passage of a solution of one salt into adjacent water or a solution of a second salt* contrary to gravity. The diffusive power varies with different bodies, and depends on the independent motions of the molecules. It varies, too, with different temperatures, warmth increasing the diffusive velocity. Equal velocities are said to be noted in the case of isomorphous salts. It is rapid with potassic chloride, and with most crystalline bodies, but slow with gelatine and with most jelly-like bodies. Bodies that diffuse rapidly are called "*crystalloids*," and bodies that diffuse slowly or not at all, "*colloids*" (κόλλα, glue). This diffusion of certain bodies and non-diffusion of others takes place equally well if a membrane, which must itself be colloidal, separates the two liquids (Dialysis), the rapidity with which one liquid passes through the membrane into the second in no way necessarily representing the rate at which the second passes through the membrane and into the first liquid.

In describing the solubility of solids, it is usual to state the number of parts of *anhydrous* salt taken up by 100 parts of water at a given temperature.

Ordinarily the solubility of a body increases as the temperature increases. If a boiling solution of a salt be allowed to cool, *exposed to the air*, a certain portion of the salt crystallizes out, and the clear solution at normal temperatures, is termed "*a saturated solution*," *i.e.*, a solution which at that temperature can dissolve no more of the salt; but if it be allowed to cool *out of contact with air*, a larger quantity of the salt is then held in solution than that indicated by the coefficient of solubility, and this is termed "*a supersaturated solution,*" from which, however, the excess of solid matter may often be separated by slight physical disturbances, such as motion, dust, or dropping into the solution a minute fragment of the salt.

A saturated solution of one salt will often dissolve an appreciable amount of a second salt.

The influence of temperature on solubility is not constant :—

(1.) The solubility, for instance, of *potassic chloride* is directly as the temperature, but the solubility of *potassic chlorate* increases far more rapidly than the temperature.

(2.) The solubility of some bodies, such as *sodic chloride*, is the same at all temperatures.

(3.) The solubility, in some cases, decreases as the water is heated. Thus *lime* is twice as soluble in water at 32° F. (0° C.) as it is in water at 212° F. (100° C.). One part of strontic sulphate requires 7,000 parts of water at 57·2° F. (14° C.) and 9,600 parts at 212° F. (100° C.) for complete solution.

(4.) Occasionally the maximum solubility of substances is at a temperature a little above the common temperature, and decreases if the temperature be raised. Thus at 32° F. (0° C.) 1 part of *calcic sulphate* is soluble in 488 parts of water, but at 95° F. (35° C.) 1 part is soluble in 393 of water. This is the point of maximum solubility of calcic sulphate in water, and from this point its solubility decreases, for, at 212° F. (100° C.) 1 part requires 460 of water for solution. Solution is usually accompanied by *contraction*, the volume of the solvent, *plus* the substance dissolved, being greater than the solution. (To this rule NH_4Cl is an exception.) It is also accompanied by the *absorption of heat*, save and except where chemical union occurs between the solvent and the substance dissolved.

Water, when "*superheated,*" *i.e.*, heated under pressure, possesses greatly increased solvent powers. Thus, at 300° F. (149° C.) water dissolves glass. Possibly the dissolved silica present in the Geyser springs, may be accounted for by the action of water, superheated by internal pressure.

II. *Solubility of liquids.*—"*Miscibility.*"—By this is implied the miscibility or the blending of liquids. Water mixes with alcohol. If the water be in excess the water is regarded as the solvent, whilst the alcohol is termed the solvent if it be in excess.

III. *Solubility of gases.*—"*Absorption.*"—All gases are more or less soluble in water—*i.e.*, are more or less *absorbed* by water—but all gases are not equally soluble.

The "*coefficient of solubility,*" or "*absorption coefficient,*" as it is called, is the volume of gas absorbed by one volume of water at 59° F. (15° C.).

The following table exhibits the absorption or solubility of various gases in water:—

Gas at 59° F. (B.P. 30).	Vol. dissolved by one vol. of water at 59° F. (15° C.) and 30 B.P.	Vol. dissolved by one vol. of water at 32° F. (0° C.) and 30 B.P.
Hydrogen	·0193	·0193
Nitrogen	·0148	·0203
Carbonic oxide	·0243	·0328
Oxygen	0·299	·0411
Marsh gas	·0·391	·0545
Olefiant gas	·1615	·2563
Nitrous oxide	·7780	1·3052
Carbonic acid	1·0000	1.7967
Chlorine..	2·5680	—
Sulphuretted hydrogen ..	3·2326	4·3706
Sulphurous acid	43·5640	68·8610
Hydrochloric acid	457·8000	505·8000
Ammonia	782·7000	1148·0000

[Note.—The absorption coefficient is often stated as the volume of gas at 0° C. and 766 mm. absorbed by 1 c.c. of liquid at 0° C. and 766 mm.]

The solubility of a gas in water (and, indeed, in all other solvents) is influenced by certain circumstances :—

(1.) *The temperature of the solvent.*—The general law may be thus stated :—*The volume of gas dissolved is constant for a given temperature, but increases as the temperature of the solvent decreases.* But note—

(*a.*) In the case of hydrogen the solubility remains the same for all temperatures.

(*β.*) The law is only true so long as the solvent remains liquid, for directly the liquid freezes the dissolved gases are *usually* liberated. But exceptions to this rule are found in certain cases, such as carbonic anhydride, and in the case of those gases such as chlorine, that form definite chemical compounds with water.

When the solvent is boiled, the dissolved gas is, as a rule, entirely evolved. In the case, however, of those gases that are very soluble (such as hydrochloric acid gas), mere boiling never effects the entire expulsion of the gas. The solution having become of a certain strength remains constant, evaporation to dryness being the only means of effecting complete removal.

(2.) *The degree of pressure.*—In the case of the moderately soluble, but not in the case of the very soluble gases, Dalton and Henry's law holds good, that *"the volume of gas absorbed varies directly with the pressure."* With a pressure, *e.g.*, of one atmosphere, one volume of water at 0° C. dissolves 1·18 volumes of CO_2; with $\frac{1}{2}$ atmosphere, $\left(\frac{1{\cdot}18}{2}=\right)0{\cdot}59$ volume ; with 2 atmospheres, (1·18 × 2=), 2·36 volumes, etc.

By placing a solution of gas in a vacuum, its almost entire removal from the solvent may be effected. It may be noted, moreover, that a similar withdrawal may often be effected by exposing the solution of one gas to an atmosphere of a second gas.

We have now to consider *the action of solvents on a mixture of gases.*—Good drinking water should be well aërated, *i.e.*, should contain a certain quantity of dissolved gas. Every gallon of water should yield about 7 cubic inches of gas (4 cubic inches of nitrogen, 2 cubic inches of oxygen, and 1 cubic inch of carbonic anhydride). These gases are dissolved by the water from the air. But air is a mixture of 1 part of oxygen to 4 parts of nitrogen (exactly as 21 to 79), whereas the dissolved gas is in the proportion of 1 of oxygen to 2 of nitrogen. How is it, then, that the ratio of the gases dissolved by the water is not the same as that in which they are present in the air?

In a mixed gas the solution of the several constituents does not depend on the *general* pressure, but on *the pressure exerted by each gas* "per se." For example, to take a simple case: If we act with water on a mixture of one volume of oxygen and three volumes of nitrogen under a pressure of four atmospheres, we shall find that the oxygen dissolved will be that quantity that the water can absorb under one atmosphere (*i.e.*, the $\frac{1}{4}$th of four atmospheres); and the nitrogen, the quantity the water can absorb under a pressure of three atmospheres (*i.e.*, $\frac{3}{4}$ths of four atmospheres). So with air, $\frac{1}{5}$th of which is oxygen and $\frac{4}{5}$ths nitrogen, the pressure of the whole being one atmosphere. The quantity of each gas dissolved will be found by multiplying the proportion of the gas in the mixture by its co-efficient of solubility; thus—

0·0299 (coefficient of absorption of oxygen) × $\frac{1}{5}$ (proportion of oxygen in air) = 0·00598
0·0141 (do. do of nitrogen) × $\frac{4}{5}$ (do. of nitrogen do.) = 0·01184

0·01782

Therefore, of every 0·01782 volumes of air dissolved by water, 0·00598 will be oxygen and 0·01184 nitrogen; that is, in about the proportion of two of nitrogen to one of oxygen. Thus the air dissolved by water is richer in oxygen than the atmosphere. This oxygen is present in the water, not only for the support of water-animal life, but for the water's purification, whereby harmful products are changed into harmless products by oxidation. The carbonic acid, too, plays its part in rock disintegration and in soil-formation.

Water dissolves *the haloid* elements, and is slowly decomposed by them with the evolution of oxygen ($H_2O + Cl_2 = 2HCl + O$). On *the combustible solids* (carbon, etc.), it has little or no action unless it be heated, when it is decomposed ($C + H_2O = CO + H_2$). On *oxygen*, *nitrogen*, and *hydrogen*, its action is simply that of a solvent. The *metals* are attacked differently by it. (i.) *The alkaline metals* decompose it at ordinary temperatures; (ii.) *magnesium*, etc., decompose it if the water be boiling; (iii.) *iron*, *zinc*, etc., decompose it when the metals are red hot; (iv.) *gold* and *platinum* require to be raised to a white heat in order to effect its decomposition.

(γ.) *Chemical.*—Water is without action either on litmus or turmeric. Chemically, it is an indifferent oxide. It unites with bodies in several ways to form hydrates. Thus—

(1.) *It unites with the anhydrides to form acids*, heat being evolved at the time of combination ($SO_3+H_2O=H_2SO_4$). This water molecule cannot be afterwards separated from the anhydride, merely by the action of heat. Sulphuric acid, moreover, has a great affinity for water, and hence one of its common laboratory uses.

(2.) *It unites with bases to form hydrates*, heat being evolved at the time of combination. In some cases the water molecule cannot be driven off by heat (*e.g.*, KHO), whilst in other cases a red heat will effect its expulsion (*e.g.*, $CaH_2O_2=CaO+H_2O$).

(3.) *It unites with certain bodies as water of crystallization, i.e.*, water connected with the shape and color of the crystals (aquates). This water of crystallization may be expelled at a temperature of 212° F. (100° C.), certain changes resulting. Thus, if blue *sulphate of copper* ($CuSO_4,5H_2O$) be heated to 212° F. (100° C.), it loses four of its water molecules, becoming $CuSO_4,H_2O$, whilst at the same time it loses both shape and color. So again the pink hydrated chloride of cobalt ($CoCl_2+6aq$) forms, when heated, the blue anhydrous chloride ($CoCl_2$), which again becomes hydrous and pink on exposure to air (sympathetic ink). Similar changes of color are well marked in magnesic-platino-cyanide, which is green, red, yellow, or white, according to the quantity of water of crystallization it contains. Some salts (as *e.g.*, NaCl) contain no water of crystallization, whilst in many others (as *e.g.*, sodic sulphate, borax, etc.), the number of water molecules may be made to vary, different crystalline shapes resulting.

In some cases (as *e.g.*, sodic carbonate) bodies part with their water of crystallization at ordinary temperatures (*effloresce*); whilst many others (as *e. g.*, potassic carbonate) absorb water on exposure, and melt (*deliquesce*). Thus calcic chloride is used in the laboratory as a desiccating agent.

(4.) *It unites in certain cases as water of constitution, or water of halhydration, i.e.*, as water associated with the chemical properties of bodies. Thus, a crystal of magnesic sulphate contains seven molecules of water ($MgSO_4,7H_2O$). If this be heated to 212° F. (100° C.), six molecules (water of crystallization) are driven off, and the salt is represented by the formula $MgSO_4,H_2O$. No heat, however, short of 410° F. (210° C.) will effect the removal of this last water molecule, and when this temperature is reached, the salt itself undergoes decomposition. It is clear, therefore, that this last water molecule, termed "*water of constitution*," is bound to the salt by a closer attraction than the other six molecules.

This molecule of constitutional water may often be replaced by another salt, whereby a double salt is formed. Thus, $MgSO_4,H_2O + 6H_2O$ may be made to form $MgSO_4,K_2SO_4 + 6H_2O$, where K_2SO_4 replaces the molecule of constitutional water.

In order to express these two forms of water in a salt, the water of constitution is often written in chemical symbol, and the water of crystallization as *aq* (*aqua*), thus, $MgSO_4H_2O + 6aq$.

(5.) Water may possibly exist in many organic bodies, such as sugar, starch, gum, etc., in a molecular form.

Varieties of Water.

I. Common Water.—(*a.*) *Rain Water.*—This is the purest form of natural water. Even in the country, however, and much more in towns and in the neighbourhood of factories, it is always more or less contaminated with the various impurities present in the air. The rain always contains more or less sodic chloride, organic matter, ammonia, nitric acid, etc. If rain water has been allowed to come into contact with lead, it is certain to dissolve a small quantity of the metal.

The rain collected after a long continuance of wet is the nearest approach known to pure natural water.

(*b.*) *Spring and Well Water.*—The total solids present in these may vary from 5 to 200 grains and more per gallon, their quantity and character being largely dependent on the chemical nature of the soil through which the water percolates. Calcic and magnesic carbonates and sulphates, and sodic chloride, are the salts most commonly present.

The presence of *nitrites* or an excess of *nitrates and chlorides,* frequently found in the shallow well waters of towns, usually indicates sewage pollution, the two first being the oxidized products of animal nitrogenized substances (ammonia and albuminoid bodies), whilst the last is derived from the common salt used as food.

Sodic carbonate is commonly found in those well waters (as in the deep wells of London) that have percolated through a bed of chalk. The organic matter in the water of wells and springs is usually very small. Carbonic acid is the chief and very often the only gas present in such waters. Its origin is, probably, either the subterranean decomposition of carbonates, or the oxidation of the carbon of organic matter. It serves to hold the earthy carbonates in solution. A spring-water will often exhibit a slight turbidity after standing, due to the carbonic acid escaping by the exposure of the water to air, with the consequent precipitation of a part of the calcic or magnesic carbonate.

The temperature of spring-water varies from ice-cold to 167° F. (75° C.), as in the case of some of the Carlsbad springs. The deep springs are usually the hottest.

(*c.*) *Lake and Marsh Water* usually contain more or less organic matter. Lake water is of excessively variable composition, being sometimes very pure, but at other times loaded with saline and organic matter.

(*d.*) *River Water.*—Its composition depends much on the nature of the soil through which the river passes, and also on the extent of motion, the nature of the bed of the river, and the exposure the water undergoes. River water may be regarded as a mixture of rain, spring, and lake water. It differs from spring water generally by being less clear (spring water undergoing natural filtration), less sparkling (the carbonic acid present being in smaller quantity), and usually by containing less solid matter. The organic matter present is derived from surface drainage and sewage; but this, after a sufficient flow, and if well diluted, is in a great measure got rid of, owing to the self-purifying action of running water.

II. Mineral Waters, *i.e.*, a spring water containing some medicinal ingredient. The names given to mineral waters depend on the predominating ingredient present; thus—

(*a.*) *Acidulous Waters*, from carbonic acid, which may be present in quantities varying from 30 to 200 cubic inches per gallon (Seltzer, Ilkeston, Spa, Pyrmont, etc.).

(*b.*) *Aperient Saline Waters*, from the presence of sulphates :—

(1.) Magnesic sulphate (Epsom, Leamington, etc.).
(2.) Sodic sulphate (Cheltenham, Scarborough, etc.).

(*c.*) *Calcareous Waters*, from calcic sulphate, or from calcic carbonate held in solution by carbonic acid (Matlock, Bath, Bristol, etc.).

(*d.*) *Chalybeate Waters*, from the presence of carbonate of iron held in solution by free carbonic acid (Pyrmont, Tunbridge, etc.). On exposure to air, Fe_2O_3, H_2O is precipitated ($2FeCO_3 + O + H_2O = Fe_2O_3, H_2O + 2CO_2$).

(*e.*) *Brine*, from the presence of sodic chloride, bromide and iodide (Middlewich, Shirleywich, Droitwich, etc.).

(*f.*) *Alkaline Waters*, from the presence of sodic carbonate and bicarbonate (Ems, Vichy, Malvern, etc.).

(*g.*) *Siliceous Waters*, from the presence of silica (Geysers).

(*h.*) *Sulphuretted* or *Hepatic Waters* (Harrogate, Aix-la-Chapelle, etc.).

(*i.*) *Sulphurous Waters* (Springs in the neighbourhood of volcanoes).

(*j.*) *Boracic Waters* (Lagoons of Tuscany).

III. Sea-Water.—Sea-water contains a large quantity of sodic and magnesic chlorides, to which its bitter saline taste is due, and to the hygroscopic character of which salts, the non-drying of clothes wetted with sea-water is to be attributed.

The following two analyses of sea-water may be quoted :—

ANALYSIS OF TWO SAMPLES OF SEA WATER TAKEN AT MARGATE, November 30th, 1882 (Tidy).

The results are stated in grains per gallon.

		High Water, 2·59 P.M. Wind N., blowing hard.	Low Water, 9.10 P.M. Wind N., slight.
Total solid matter		2340·4	2250·0
Ammonia		0	0
Organic carbon		0·274	0·282
Organic nitrogen		0·249	0·275
Free oxygen (cubic inch)		1·656	1·65
Lime		24·62	18·07
Magnesia		143·92	140·10
Chlorine		1239·38	1228·96
Nitrogen (as nitrates)		0	0
Silica		0·32	0·60
Suspended matter	Mineral, per cent.	11·24 { 77·5 %	16·43 { 74·67 %
	Organic, ,,	22·5 %	25·33 %
Hardness, before boiling, degrees		395°	388°

The sea is the receptacle for the solid matters discharged by rivers, and dissolved by them from the earth. Their abstraction again from the sea, and their return to the soil, is effected by fish and marine plants.

IV. Water for Drinking Purposes.—It is important to determine—

(1.) *Hardness.*—The terms "hard" and "soft," refer to the soap-destroying power of a water. Soap is an *alkaline stearate.* The addition to it of lime and magnesia decompose it, forming a *calcic* or *magnesic stearate.* Hence the reason why it is difficult to obtain "a lather" with hard water (*i.e.*, a water containing lime and magnesian salts), viz., because a certain quantity of the soap is required to decompose the calcic and magnesian salts before a lather can be obtained, whilst, conversely, a lather is at once formed with a soft water, because of the absence of calcic and magnesic salts. Two kinds of hardness are usually described—(α.) *Temporary hardness, i.e., hardness due to calcic or magnesic carbonates.* These salts are almost insoluble in pure water, but are freely soluble in water containing carbonic acid (possibly as bicarbonates). On boiling, the carbonic acid is expelled and the carbonates are precipitated. Hence *temporary hardness* is that hardness which may be got rid of by boiling the water. (β.) *Permanent hardness, i.e., hardness due to calcic and magnesic sulphates,* etc. This is not got rid of by boiling. By the terms "*total*" or "*initial hardness*" we imply both the temporary and permanent hardness of a water.

In expressing the hardness of a water in degrees, it is to be understood that every degree, theoretically, represents 1 grain of calcic carbonate or its equivalent in soap-destroying power, in one gallon of water.

(2.) *Action on lead.*

(3.) *Presence of organic matter.*

Hydric Peroxide (H_2O_2).

Molecular weight (probable), 33·92.

Synonyms.—*Peroxide of Hydrogen; Hydric Dioxide; Hydroxyl; Oxygenated Water.*

History.—Discovered by Thénard in 1818. Examined by Brodie and by Schönbein in 1850.

Natural History.—The atmosphere, dew, rain and snow contain small quantities.

Preparation.—(1.) Peroxide of barium (BaO_2), (prepared by heating caustic baryta (BaO) in a current of oxygen) is made into a paste with water ($BaO_2,6H_2O$ being formed), and added to dilute hydrochloric acid, in a vessel surrounded by a freezing mixture:—

$$\underset{\text{Hydrated baric peroxide}}{BaO_2,6H_2O} + \underset{\text{Hydrochloric acid}}{2HCl} = \underset{\text{Hydric peroxide}}{H_2O_2} + \underset{\text{Water}}{6H_2O} + \underset{\text{Baric chloride.}}{BaCl_2.}$$

By decomposing the $BaCl_2$ thus formed, with dilute sulphuric acid, HCl will be set free. More of the baric peroxide may then be added, until the solution of H_2O_2 is of the required strength. The hydrochloric acid may be removed by argentic sulphate, and the sulphuric acid by baryta water. Finally, the solution is to be concentrated by slow evaporation 'in vacuo' over sulphuric acid.

(2.) By passing carbonic anhydride through a mixture of water and baric peroxide, or by adding BaO_2 to dilute hydrofluoric acid, a baric carbonate or fluoride, as the case may be, being precipitated; or by adding potassic peroxide to a tartaric acid solution, under which circumstances a potassic tartrate will be precipitated:—

$$\underset{\text{Baric peroxide}}{BaO_2} + \underset{\text{Carbonic anhydride}}{CO_2} + \underset{\text{Water}}{H_2O} = \underset{\text{Baric carbonate}}{BaCO_3} + \underset{\text{Hydric peroxide.}}{H_2O_2.}$$

Properties.—(*a.*) *Sensible and physiological.* A colorless, and when concentrated, a syrupy liquid, having a slight chlorous odor. It whitens and blisters the skin. It has a powerfully metallic, astringent taste, whitening and deadening the sensibility of the tongue, and rendering the saliva thick and viscid.

(*β.*) *Physical.* Specific gravity, 1·453. A temperature of 70° F. (21·1° C.) effects its slow decomposition into water and oxygen, a violent explosion occurring at 212° F. (100° C.), when the liquid evolves 475 times its volume of oxygen, the theoretical quantity being

501·8 vols. It does not freeze at —22° F. (—30° C.). It mixes with water in all proportions, and is soluble in ether, which will extract it from its aqueous solution when shaken up with it.

(γ.) *Chemical.* Its reaction is neutral, but it bleaches litmus.

A dilute solution is more stable than a stronger one. Thus, a weak solution may, to a certain point, be concentrated by boiling, some undecomposed H_2O_2 passing over along with the steam. The ethereal solution may be distilled without decomposition.

In contact with ozone, water is produced, and common oxygen set free. It forms water when acted on with nascent hydrogen ($H_2O_2 + Zn + H_2SO_4 = ZnSO_4 + 2H_2O$). It undergoes slow spontaneous decomposition, evolving oxygen, leaving common water. (This action is retarded by the presence of acids, and hastened by alkalies.) Its decomposition may be effected by the presence of certain powdered metals, such as gold, silver, platinum, etc., the metals themselves undergoing no change during the process. (*See* CATALYSIS.) A similar result occurs with finely divided carbon. Iron, tin, and antimony have no action upon it. As a chemical agent, hydroxyl has both oxidizing and reducing properties :—

(1.) *Oxidizing.* It bleaches litmus and indigo. It rapidly changes selenium, arsenicum, etc., into their highest oxides, with evolution of heat and light. It converts arsenious and sulphurous acids into arsenic and sulphuric acids ; sulphide into sulphate of lead; the protoxides of iron, cobalt, calcium, etc., into peroxides, etc., etc. It bleaches many organic bodies, changing, *e.g.*, dark hair to a golden tint (auricome). The bleaching action of hydroxyl (like that of chlorine) is the result of its oxidizing power.

(2.) *Deoxidizing* (*Reducing*). Mixed with the protoxides of silver, mercury, gold, etc., the hydroxyl not only loses its own oxygen, but also effects the reduction of the oxide ($Ag_2O + 2H_2O_2 = Ag_2 + H_2O + O_2$). Similarly it reduces the peroxides of manganese, lead, etc. ($MnO_2 + H_2O_2 = MnO + H_2O + O_2$), and also chromic and permanganic acids ($2CrO_3 + 3H_2O_2 = Cr_2O_3 + 3H_2O + 3O_2$), it being at the same time itself reduced. Thus an atom of oxygen from the hydroxyl combines with an atom from the compound, with which it is only feebly united, to form an oxygen molecule (O_2). For the same reason hydroxyl and ozone effect mutual decomposition, with the liberation of oxygen and the formation of water. For this reason H_2O_2 was at one time termed *antozone* ($H_2O_2 + O_3 = H_2O + 2O_2$).

It is to be noted that in all these cases the action is retarded by the presence of an acid, and assisted by the presence of a free alkali.

Tests.—(1.) It, like other oxidizing agents, liberates iodine from potassic iodide. ($H_2O_2 + 2KI = 2KHO + I_2$.) *Delicacy:* 1 part in 25 millions. Unlike other oxidizing agents, however, it is capable of effecting this liberation in the presence of ferrous sulphate.

(2.) Added to a solution of guaiacum mixed with blood corpuscles it turns it of a blue color. (Schönbein.)

(3.) If chromic anhydride (CrO_3) or a few drops of potassic bichromate acidulated with sulphuric acid, be added to a solution of hydric peroxide, an unstable perchromic oxide is first formed, Cr_2O_3 being the ultimate product. This compound (perchromic acid) is of a blue color. It is soluble in ether, by which its removal from the solution may be effected. This constitutes a very delicate test for hydroxyl, no other known substance effecting the oxidation of chromic to perchromic acid.

(4.) Hydroxyl may be estimated (if nitrites and organic matter be absent) by the addition of a standard potassic permanganate solution to an acid solution of the peroxide ($2KMnO_4 + 3H_2SO_4 + H_2O_2 = K_2SO_4 + 2MnSO_4 + 4H_2O + 3O_2$).

Uses.—It has been used in medicine externally as a lotion, and internally for diabetes and oxaluria. It constitutes the golden hair dye of the shops, the dyeing action being in reality a bleaching (oxidizing) action. It is also used for bleaching and cleansing oil paintings (converting PbS into $PbSO_4$) and stained engravings.

COMPOUNDS OF HYDROGEN AND THE HALOID ELEMENTS.

Hydrochloric Acid (HCl) (*Anhydrous*).

Molecular weight, 36·5. *Molecular volume*, ☐☐. *Relative weight* 18·25. *Specific gravity*, 1·247. *Theoretic specific gravity* ($18·25 \times 0·0693$) = 1·264. 1 *litre weighs* 18·25 *criths* ($0·0896 \times 18·25$) 1·635 *grms. and* 100 *cubic inches* 39·00 *grains.*

Synonyms.—*Spirit of Salts; Marine acid; Muriatic acid; Chloride of Hydrogen; Chlorhydric acid.*

History.—Probably known to Geber in the eighth century. The process of obtaining it from sulphuric acid and salt was first described by Glauber. Priestley (1772) was the first who obtained it as a gas. Its real nature was suspected by Scheele (1774), but it was believed by Berthollet and others to be an element, until Davy (1810) established the truth of Scheele's suspicions.

Natural History.—It is not found either in the animal or in the vegetable kingdom. It is found in the gases issuing from volcanoes, and in springs and rivers in their vicinity. It is found in the air over the sea, and in the neighbourhood of alkali works, etc.

Preparation.—(1.) By the direct combination of equal volumes of hydrogen and chlorine by heat, light, or electricity. Combination does not take place when the mixed gases are kept in the dark. In diffuse daylight combination is slow, whilst in sunlight it is often accompanied by explosion.

(2.) By burning hydrogen in chlorine.

(3.) By the action of dilute sulphuric acid on chlorides.

(*a.*) Prepared by this method in the laboratory in glass retorts *at a low temperature* the reaction is as follows :—

$$H_2SO_4 + NaCl = NaHSO_4 + HCl.$$

Sulphuric acid + Sodic chloride = Hydric sodic sulphate + Hydrochloric acid.

(*β.*) It is usually prepared for commercial purposes in iron retorts *at a high temperature*, when the following reaction occurs with the formation of the normal sulphate :—

$$H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl.$$

Sulphuric acid + Sodic chloride = Sodic sulphate + Hydrochloric acid.

(*Confer* Salt Cake.)

(4.) By passing steam and chlorine through a red-hot porcelain tube ($2H_2O + 2Cl_2 = 4HCl + O_2$).

Properties.—(*a.*) *Sensible and physiological.*—A colorless, pungent-smelling gas, burning in the air, and having a strong acid taste. It is poisonous to animal life and destructive to vegetation, even when diluted with 25,000 parts of air.

(*b.*) *Physical.*—Specific gravity 1·247 ; 100 cub. in. (at 60° F. and 30 Bar. Pr.) weigh 39·00 grains, and 1 litre (0° C. and 760 mm.) 1·6352 grm. At a pressure of forty atmospheres at 50° F. (10° C.) it forms a colorless liquid, having a specific gravity of 1·27, the liquid being less refracting than water. It solidifies at a cold of —177° F. (—116° C.), and melts at —152·5° F. (—112·5° C.).

The gas may be decomposed by electricity.

(*c.*) *Chemical.*—Its composition may be proved synthetically by direct combination, and analytically by heating a piece of sodium, or agitating some sodium amalgam in a known volume of the gas, and measuring the residual gas (hydrogen). Hydrochloric acid gas reddens litmus. It neither supports the combustion of a taper, nor is itself combustible. Sodium and potassium burn in it. It acts on the metals, evolving hydrogen. It dissolves bitumen. It fumes in the air owing to its affinity for water, which absorbs 500 times its bulk at 32° F. (0° C.), and 418 volumes at 50° F. (10° C.). The solution of the gas forms the ordinary hydrochloric acid of the laboratory. One volume of alcohol (sp. gr. 0·836) absorbs 327 volumes of the gas.

The liquefied hydrochloric acid (anhydrous) dissolves solid litmus without reddening it, and, unlike the solution of the gas, is without action on iron, zinc, or lime, and even upon the carbonates.

Hydrochloric Acid (*Solution*).

Preparation.—By dissolving the gas in water.

Properties.—(*a.*) *Physical.* The liquid is colorless if pure, but more often it is slightly yellow. It fumes in the air. A solution containing *more* than 20 per cent. of HCl, evolves when heated hydrochloric acid gas; but if it contains *less* than 20 per cent., it then merely gives off water until it becomes a 20 per cent. solution. A 20 per cent. acid ($HCl,8H_2O$) distils unchanged at 230° F. (110° C.), at normal pressure. Different strengths of acid, however, may be obtained at varying pressures. The lower the pressure, the greater the percentage of HCl remaining in the residual acid. By electrolysis it may be split up into its constituent gases.

Its specific gravity varies with its strength. (See Table III. in Appendix.) The fuming acid at 59° F. (15° C.) has a sp. gr. of 1·21, and contains 43 per cent. of HCl.

(β.) *Chemical.* A weak solution of the acid turns blue litmus red. Its action on the metals varies. Some metals are freely dissolved by the cold acid with the evolution of hydrogen (K, Na, Ba, Fe, Zn, etc.);—others are only acted on by the boiling acid (Sn, Cu);—others are only slightly acted upon (Sb, Pb, Ag, Bi, etc.)—whilst some are perfectly unaffected, either by the cold or by the boiling acid (Au, Pt, etc.). If, however, free chlorine be present in the acid solution, both gold and platinum are rapidly dissolved by it. On the *metallic oxides* it commonly forms water with a chloride of the metal corresponding to the oxide acted upon ($Fe_2O_3 + 6HCl = Fe_2Cl_6 + 3H_2O$), or if such compound does not exist, to one containing less chlorine than its equivalent oxygen ($PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$).

IMPURITIES.

(1.) *Sulphurous acid;* derived from the deoxidation of the sulphuric acid, either by the organic matter of the salt, or by the metal of the still.

Test.—The evolution of sulphuretted hydrogen when zinc is added to the acid.

(2.) *Sulphuric acid;* known by a soluble baryta salt producing a white precipitate of $BaSO_4$ in the diluted acid.

(3.) *Free chlorine,* which imparts a greenish-yellow tint to the acid solution, may be known by its odor, and by the solution dissolving a little piece of gold leaf.

(4.) *Iodine* and *bromine* are sometimes present, derived from impurities in the common salt.

(5.) *Arsenious chloride,* derived from the sulphuric acid, may be known by the acid giving a yellow precipitate with sulphuretted hydrogen.

(6.) *Stannic chloride* (mentioned by Gmelin) will be thrown down as a yellow precipitate, gradually becoming brown on passing sulphuretted hydrogen through the acid.

(7.) *Plumbic chloride* (Vogel) may be present, derived from the lead in the sulphuric acid, as well as possibly from other sources.

(8.) *Ferric chloride* (Rose and Graham) may be recognised by neutralising the acid with sodic carbonate and afterwards adding tincture of galls or potassic ferrocyanide. With the former a violet, and with the latter a blue precipitate will be obtained.

(9.) *Other salts* may be recognised by evaporating the acid to dryness, and examining the residue.

(10.) *Organic matter.* This is often the cause of the dark color of the acid. It may be known by evaporating the acid to dryness, and noting whether the residue becomes charred by the continued application of heat.

PREPARATION OF PURE HYDROCHLORIC ACID.

It will at all times be found easier to *make* a pure acid, than to *purify* a bad one. The following method is recommended :—Dilute one part of good sulphuric acid with six parts of water, and pass a stream of well-washed sulphuretted hydrogen through it for some hours. After allowing it to stand undisturbed for five or six days, so that any precipitate may settle, syphon off the supernatant acid, and having added a teaspoonful of common salt, concentrate by heat to the original bulk.

Fill a large retort half full of good salt, and add to it the sulphuric acid thus prepared. The retort should have fitted to it a glass tube, of such length and shape that it may pass into a pint bottle half full of distilled water, the end of the tube dipping about $\frac{1}{8}$ of an inch under the water. The bottle is to be fitted with a second tube, connected with a second bottle of water, so that any acid vapors that escape from the water of the first bottle may be absorbed by the water of the second. The acid thus obtained will generally be found pure, but should be carefully tested before using, both by passing sulphuretted hydrogen through it, as well as by boiling with copper, the purity of which has been previously proved by analysis.

Characters of pure hydrochloric acid :—

(1.) The absence of color (freedom from organic matter).

(2.) The absence of residue on evaporation to dryness (freedom from metallic salts, etc.).

(3.) No precipitate on the addition of an excess of ammonia (freedom from iron).

(4.) No precipitate with sulphuretted hydrogen (freedom from arsenic, and from sulphurous acid).

(5.) No precipitate in a dilute solution with baric chloride (freedom from sulphuric acid).

Hydrobromic Acid (HBr) (*Anhydrous*).

Molecular weight, 81. *Molecular volume,* ☐☐. *Specific gravity,* 2·75 —100 *cubic inches weigh* 86·79 *grains.*

Synonym.—*Hydric bromide.*

History.—Discovered by Balard in 1826.

Preparation.—(1.) By the direct union of hydrogen and bromine vapor: such as by burning hydrogen in a mixture of air and bromine vapor. Also by combining hydrogen and bromine vapor either by means of electric sparks, or by contact of heated platinum, or by their passage through a red-hot tube ($H_2 + Br_2 = 2HBr$).

(2.) By heating potassic or sodic bromide with phosphoric acid:—

$$3KBr + H_3PO_4 = K_3PO_4 + 3HBr.$$

Potassic bromide + Phosphoric acid = Potassic phosphate + Hydrobromic acid.

[N.B.—If sulphuric acid be used instead of phosphoric acid, the liberated hydrobromic acid both decomposes, and is decomposed by, the sulphuric acid, sulphurous acid and bromine being liberated ($2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O$).]

(3.) By distilling together bromine, water and phosphorus. The experiment is best made by dropping bromine into water in which some amorphous phosphorus is suspended. (In this reaction a phosphorous tribromide (PBr_3) is first formed.)

$$6H_2O + 3Br_2 + P_2 = 6HBr + 2H_3PO_3$$

Water + Bromine + Phosphorus = Hydrobromic acid + Phosphorous acid.

(4.) A solution of the gas may be prepared—

By passing sulphuretted hydrogen through bromine water—

$$2H_2S + 2Br_2 = 4HBr + S_2.$$

Sulphuretted hydrogen + Bromine = Hydrobromic acid + Sulphur.

Properties.—(*a.*) *Sensible and physiological.* Hydrobromic acid is a colorless, pungent and acrid gas. It is irrespirable, producing, even when very dilute, intense pulmonic irritation.

(β.) *Physical.* Specific gravity 2·75. It is not decomposed by heat. It may be condensed at —92·2° F. (—69° C.) to a liquid, and at —121° F. (—85° C.) to a solid. It is soluble in its own weight of water (*see below*).

(γ.) *Chemical.* The composition of the gas may be determined by a similar method to that described in the case of HCl (page 251). It reddens litmus. It neither burns nor supports combustion. It fumes in moist air with the liberation of a trace of bromine. Most metals are acted upon by it; thus potassium instantly decomposes it with the liberation of hydrogen. Like hydrochloric acid it is decomposed by metallic peroxides, and also by high oxygen acids. It is also decomposed by chlorine ($2HBr + Cl_2 = 2HCl + Br_2$).

Hydrobromic Acid (*Solution*).

The acid is a solution of the gas in water. A saturated solution has a specific gravity of 1·78. The solution ($HBr,5H_2O$) containing 48·17 of HBr has a specific gravity of 1·49 and boils at258·8° F. (126° C.). If an acid contain *more* than 48 per cent., when heated it parts with the gas until it becomes a 48 per cent. solution, whilst if it contain *less* than 48 per cent. it undergoes concentration till it reaches 48 per cent. At this concentration the acid may be distilled without change. It fumes when exposed to the air, a little bromine being liberated.

Hydriodic Acid (HI) (*Anhydrous*).

Molecular weight, 128. *Specific gravity* 4·4. *Molecular volume.* ☐☐.
100 *cubic inches weigh* 137·15 *grains.*

Synonym.—*Hydric iodide.*

History.—Discovered by Gay Lussac and Davy in 1814.

Preparation.—(N.B.—Note similarity in the preparation of hydriodic and hydrobromic acids.)

(1.) By the *direct union* of hydrogen and iodine vapor during their passage over spongy platinum, or through a red-hot tube ($H_2 + I_2 = 2HI$).

(2.) By heating together potassic iodide (or any other iodide) and phosphoric acid. (For similar reasons, as in the case of hydrobromic acid, sulphuric acid cannot be used in this reaction):—

$$3KI + H_3PO_4 = 3HI + K_3PO_4$$

Potassic iodide + Phosphoric acid = Hydriodic acid + Potassic phosphate.

(3.) By distilling together iodine, water and phosphorus. (In this reaction a phosphorous triiodide (PI_3) is first formed):—

$$6H_2O + 3I_2 + P_2 = 6HI + 2H_3PO_3$$

Water + Iodine + Phosphorus = Hydriodic acid + Phosphorous acid.

(4.) By heating a mixture of phosphorus, iodine, potassic iodide and water. This reaction occurs in two stages:—

(*α*.) Phosphoric acid and hydriodic acid are formed—

$$8H_2O + 5I_2 + P_2 = 10HI + 2H_3PO_4.$$

Water + Iodine + Phosphorus = Hydriodic acid + Phosphoric acid.

(*β*.) The potassic iodide is then acted upon by the phosphoric acid whereby a further quantity of HI is formed:—

$$4KI + 2H_3PO_4 = 4HI + 2K_2HPO_4.$$

Potassic iodide + Phosphoric acid = Hydriodic acid + Hydric potassic phosphate.

(5.) A solution of the gas may be prepared as follows:—

By passing sulphuretted hydrogen through iodine suspended in water—

$$2H_2S + 2I_2 = 4HI + S_2.$$

Sulphuretted hydrogen + Iodine = Hydriodic acid + Sulphur.

On distillation pure hydriodic acid may be obtained.

Properties.—(*α*.) *Sensible and Physiological.* Hydriodic acid is a colorless gas, having a strong odor and taste. It is quite irrespirable.

(*β*.) *Physical.* Specific gravity 4·4. It may be liquefied by a pressure of four atmospheres at 32° F. (0° C.). By a cold of —60° F.

(—51° C.) it solidifies to an ice-like mass. It is decomposed by heat (a hot glass rod sufficing) and by electricity. It is very soluble in water.

(γ.) *Chemical.* Hydriodic acid reddens litmus. It neither burns nor supports combustion. It is decomposed by chlorine, by bromine and by sulphurous acid, iodine being set free ((α.) $2HI + Cl_2 = 2HCl + I_2$; (β.) $4HI + SO_2 = 2H_2O + S + 2I_2$). The gas fumes in air, atmospheric oxygen slowly effecting its complete decomposition ($4HI + O_2 = 2H_2O + 2I_2$). For this reason (viz., its liability to part with hydrogen) hydriodic acid is a powerful *reducing* agent, even to the conversion of sulphuric acid into sulphuretted hydrogen ($H_2SO_4 + 8HI = H_2S + 4H_2O + 4I_2$). It is decomposed by most metals, hydrogen being set free ($2HI + 2Hg = Hg_2I_2 + H_2$). With most oxides and other salts it forms iodides ($AgCl + HI = AgI + HCl$).

Hydriodic Acid ($HI(H_2O)_n$) (*Solution*).

This is a solution of the gas in water. Saturated at 32° F. (0° C.), the solution has a specific gravity of 2. The strongest solution obtained by distillation ($2HI$, $11H_2O$) has a specific gravity of 1·7, contains 57·7 per cent. of HI, and distils unchanged at 261° F. (127° C.). It dissolves iodine. The clear and colorless solution is decomposed by atmospheric oxygen, iodine being deposited in fine crystals ($4HI + O_2 = 2H_2O + 2I_2$). The reactions of the gas given above apply equally to its reactions in solution.

Hydrofluoric Acid (HF) (*Anhydrous*).

Molecular weight (*at* 100° C.), 20. [*At* 77° F. (25° C.) *the molecular weight is* 40 (H_2F_2).] *Molecular volume,* ☐☐. *Specific gravity of vapor*, 0·693 ; *of liquid at* 55° F. (12·8° C.), 0·987.

Synonym.—*Hydric fluoride.*

History.—Discovered by Scheele (1772). Examined by Gay Lussac and Thénard (1810), Fremy and Gore (1869).

Preparation.—(1.) By the action of hydrogen on dry silver fluoride.

(2.) The anhydrous acid may be prepared by heating fused fluoride of hydrogen and potassium (HF.KF), in a platinum retort, and condensing the anhydrous acid which distils over in a platinum receiver surrounded by a freezing mixture.

Properties.—(α.) *Physical.* The anhydrous acid is a colorless, fuming liquid, which boils at about 65° F. (18·3° C.), and has a specific gravity of 0·987 at 55° F. (12·8° C.). It does not solidify at —30° F. (—34·5° C.). The anhydrous liquid acid is said neither to have any action on glass nor on the metals, excepting upon sodium and potassium, which dissolve in it, evolving hydrogen. It chars organic substances, burns the skin, and explodes when mixed with oil of turpentine. When electrolysed with platinum electrodes hydrogen is evolved at the negative pole, and a fluoride of platinum formed at the positive pole.

Hydrofluoric Acid ($HF(H_2O)_n$) (*Solution*).

This consists of a solution of the anhydrous acid in water, with which it combines with intense avidity.

Preparation.—(1.) By heating together calcic fluoride and sulphuric acid in a lead or platinum retort, and either passing the gas into water, or condensing the distillate in a receiver surrounded by a freezing mixture :—

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4$$

Calcic fluoride + Sulphuric acid = Hydrofluoric acid + Calcic sulphate.

Properties.—(*a.*) *Physical.*—A colorless, strongly corrosive liquid. The concentrated acid has a specific gravity of 1·060, which by sufficient dilution to form the acid $HF,2H_2O$, rises to a specific gravity of 1·150, but decreases on further dilution. The acid $HF,2H_2O$ boils at 248° F. (120° C.), and distils unchanged.

(*β.*) *Chemical.*—The acid solution fumes in air from its affinity for water. It reddens litmus. It acts powerfully on all organic substances, explodes when mixed with turpentine, and dissolves most metals (except Au, Pt, Ag, Hg, Pb, and Mg) evolving hydrogen and forming metallic fluorides ($Fe+2HF=FeF_2+H_2$). It dissolves glass, forming a fluoride of silicon (SiF_4), and must therefore be preserved in gutta-percha bottles ($SiO_2+4HF=SiF_4+2H_2O$). [Gore states that perfectly pure and *dry* hydrofluoric acid has no action on glass.] It is not decomposed by chlorine.

Test.—Its corrosive action on glass.

Hydrofluosilicic Acid ($2HF,SiF_4$ or H_2SiF_6).

Synonym.—*Silicofluoric acid.*

Preparation.—By the action of water on silicic fluoride ($3SiF_4+4H_2O = H_4SiO_4+2H_2SiF_6$).

Properties.—The solution (in which condition only it is known) is a fuming acid liquid. It does not attack glass. When heated, silicic fluoride is evolved, and hydrofluoric acid, which readily dissolves glass, remains in solution.

Neutralised with bases, a fluosilicate is formed ($2KHO+2HF,SiF_4=2H_2O+2KF,SiF_4$); but if the base be added in excess, silica is thrown down, and a metallic fluoride produced ($6KHO+2HF,SiF_4=4H_2O+6KF+SiO_2$). The baric ($BaSiF_6$) and potassic fluo-silicates (K_2SiF_6) are very insoluble.

General Review of the Compounds of Hydrogen and the Haloids.

(1.) **Constitution.**—They are all formed by the combination of 1 volume of hydrogen and 1 volume of the haloid element without condensation.

(2.) **Natural History.**—None have been found in nature in a free state, except hydrochloric acid, a trace of which has been recorded in the atmosphere in the neighbourhood of volcanoes.

(3.) **Preparation.**—HCl and HF are prepared by the action of H_2SO_4 on a chloride or fluoride. HBr and HI are prepared by the action of phosphorus on the haloid element in the presence of water, a teriodide (PI_3), or a terbromide (PBr_3) being first formed, and afterwards decomposed by the water—

$$\begin{matrix} PI_3 \\ PBr_3 \end{matrix} + 3H_2O = \begin{matrix} 3HI \\ 3HBr \end{matrix} + H_3PO_3.$$

(4.) **Properties.**—(*a.*) *Sensible and physiological.*—They are all colorless gases, having pungent odors, and producing excessive irritation when breathed. (*β.*) *Physical.* Their specific gravities vary. They may all be condensed by cold and pressure, and decomposed by heat and electricity. They are all soluble in water, forming the liquid (or rather solution of the) acid. (*γ.*) *Chemical.* They are all acid to litmus, non-combustible and non-supporters of combustion, decomposed by nitric acid, attacked by metallic peroxides, and capable of combination with bases to form salts.

COMPOUNDS OF HYDROGEN AND NITROGEN.

Theoretically there are four compounds of nitrogen and hydrogen, viz.:—

Imidogen (Laurent)	NH.
Amidogen (Kane and Dumas) ...	NH_2.
Ammonia (all chemists)	NH_3.
Ammonium (Berzelius)	NH_4.

Only one of these compounds, however, viz., ammonia, has been obtained in a free state.

Imidogen (NH).—The Imides.

The imaginary radical Imidogen was supposed to exist in certain conjugate bodies, termed by Laurent '*The Imides.*' They are not a numerous class, and are obtained by the action of heat on certain acid salts of ammonia, whereby two molecules of water are liberated. Thus $C_{10}H_{14}O_2,NH$ represents camphor imide, and is formed by abstracting two molecules of water from the bicamphorate of ammonia ($NH_4HC_{10}H_{14}O_4$).

Amidogen (NH_2).—The Amides.

Amidogen is regarded as the radical of a compound, where one hydrogen atom of ammonia has been replaced by a metal or by a compound radical. Thus, if potassium be heated in dry ammonia gas, hydrogen is liberated, and potassic amide KH_2N is formed ; or if ammonic oxalate $[(NH_4)_2C_2O_4]$ be heated, two water molecules are evolved, and oxamide $(NH_2)_2\,C_2O_2$ is left.

Two views have been entertained as to the constitution of the amides. Some regard them (1) as compounds of amidogen (NH_2) with a metal or compound radical, and others (2) as an ammonia, where a metal or a compound group has been substituted for a hydrogen atom.

Ammonia, NH_3.

Molecular weight, 17. *Molecular volume,* $\boxed{}\boxed{}$. *Relative weight,* 8·5. *Specific gravity of the gas,* 0·59, *and of the liquid,* 0·623. *Melting point of liquid,* —103° F. (—75° C.). *Boiling point,* —37° F. (—38° C.). 1 *litre of gas weighs* 0·761 *grm., and* 100 *cubic inches,* 18·21 *grains.*

Synonyms.—*Volatile Alkali ; Spirit of Urine ; Spirit of Hartshorn; Alkaline Air* (Priestley).

History.—Mentioned by Pliny. Sal ammoniac was first obtained in Libya, near the temple of Jupiter Ammon. It was first described accurately by Black (1756), and afterwards experimented upon by Priestley (1790). Its composition was determined by Berthollet.

Natural History.—It is found (α) in the *mineral* kingdom in air (about 1 in 28 million volumes), in water and in the soil ; and (β) in the *organic* kingdoms in various secretions, such as urine, etc.

Preparation.—(1.) By the direct union of hydrogen and nitrogen by silent electrical discharges (Donkin).

(2.) By the action of nascent hydrogen on nitrogen ; as, *e. g.*—

(α.) By decomposing water containing air in solution, either by a battery or with certain metals, such as iron, zinc, etc.

[Iron in rusting decomposes the moisture of the air, the free hydrogen of which combines with atmospheric nitrogen. Hence in all rust a certain amount of ammonia is to be found.]

(β.) By liberating hydrogen in the presence of nitrates or of nitric or nitrous acids ($HNO_3 + 4H_2 = NH_3 + 3H_2O$) by such means as the following :—

(i.) By acting on a solution of a nitrate with metallic aluminium and caustic soda. (Schultze.)

(ii.) By acting on a solution of a nitrate with zinc and hydrochloric acid or dilute sulphuric acid.

(iii.) If nitric oxide be passed over a mixture of lime and potassic hydrate, calcic and potassic nitrates are formed together with ammonia.

Similarly, if nitric oxide and hydrogen be passed over warm platinised asbestos, water and ammonia are formed.

(3.) By the decomposition of organic matters containing nitrogen. This may be—

(α.) *Spontaneous*, as when organic matter decays ; or

(β.) The result of *destructive distillation;* as *e.g.*, by heating horn, coal, etc., in closed retorts. Thus, most of the commercial salts of ammonia are derived from the ammoniacal liquor produced during the distillation of coal.

[Note.—The nitrogen of all nitrogenised bodies (provided it be not present as a nitrate or cyanide) is evolved as ammonia when heated with the hydrated alkalies.]

(4.) By acting on ammoniacal salts with an alkali or alkaline earth:—

$$\underset{\text{Ammonic chloride}}{2NH_4Cl} + \underset{\text{Lime}}{CaO} = \underset{\text{Calcic chloride}}{CaCl_2} + \underset{\text{Ammonia}}{2NH_3} + \underset{\text{Water.}}{H_2O.}$$

Properties.—(α.) *Sensible and physiological.* A colorless gas, having a pungent odor, and an acrid taste. When the concentrated gas is inhaled it is poisonous, but when dilute its action is stimulating.

(β.) *Physical.* The specific gravity of ammonia gas is 0·59.

By a cold of —40° F. (—40° C.), or by a pressure of 6 atmospheres at 50° F.(10° C.), or of 8·5 atmospheres at 68° F. (20° C.), the gas may be condensed into a clear, mobile, highly refractive liquid, which has a sp. gr. of 0·623, and boils at —37° F. (—38° C.). The liquid ammonia may be prepared by heating the argentic or the calcic ammonio-chloride in a sealed and bent tube. It dissolves sulphur, phosphorus, iodine, and the alkaline metals, forming with these last a blue solution, from which the metal may be deposited unchanged when the ammonia is evaporated. At a cold of —103° F. (—75° C.), the liquid ammonia freezes to an ice-like solid, having a greater specific gravity than the liquid.

In "*Carré's ice-making apparatus*" liquid ammonia is first formed in a strong iron vessel. This, on again assuming a vaporous form, absorbs sufficient heat to freeze the water with which the liquid ammonia is surrounded.

Ammonia gas may be decomposed either by electric sparks or by passing it through a red-hot porcelain tube. In each case the volume of gas formed is double the original volume operated on. Ammonia gas is very readily absorbed by clay and peaty soils, by most porous bodies, by water (more freely indeed than any other gas), and by alcohol. No definite combination of water and ammonia is known to occur, the absorption being a mere physical act of solution.

(γ.) *Chemical.* The composition of ammonia may be demonstrated by decomposing by electric sparks a given volume of the gas contained in a eudiometer over mercury, adding to the measured products an excess of oxygen, and exploding. (Page 42.)

Ammonia has an alkaline reaction ; turmeric is turned brown by it, and red litmus blue, but the changes are not permanent (volatile alkali). It is not a supporter of combustion, and is very feebly combustible, burning under favorable conditions (such as when mixed with oxygen, or by its combustion in heated air), with a greenish-yellow flame, water and free nitrogen being the products.

Action of Oxygen.—When 3 to 4 parts of ammonia gas are mixed with 1 part of oxygen it explodes, water, nitrogen, and traces of nitric acid being formed. If ozonized air be mixed with ammonia gas, white clouds of ammonic nitrite are formed, from the ammonia becoming oxidised to nitrous acid ($4NH_3 + 3O_2 = 2(NH_4,NO_2) + 2H_2O$). This oxidation of ammonia may also be effected by a hot platinum wire introduced into a mixture of the gas and air. In the presence of a strong base, the oxidation of ammonia to nitric acid and its subsequent combination with the base, constitutes the process termed *nitrification* ($2NH_3 + K_2O + 4O_2 = 2KNO_3 + 3H_2O$).

When passed over red-hot carbon, ammonic cyanide together with free hydrogen are formed ($2NH_3 + C = NH_4CN + H_2$).

Action of the haloids.—Ammonia is decomposed by the haloid elements ($8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$). If the chlorine or iodine be in excess, explosive compounds (NCl_3 or NI_3) are formed. With *acids*, ammonia forms salts. Thus when the volatile hydrochloric acid is brought near ammonia, white fumes of ammonic chloride are produced, a reaction constituting a test for the presence of the alkali. The *alkalies* have no action upon it.

Action on metallic salts.—Ammonia combines with various metallic salts. At times they apparently take the place of the water of crystallisation, although the analogy is not necessarily complete, so far as relationship between the number of the molecules is concerned. Thus, cupric sulphate has the formula $CuSO_4,5H_2O$, and ammoniated cupric sulphate the formula $CuSO_4,4H_3N,H_2O$. Hence ammonia frequently acts on metallic salts differently to potassic or sodic hydrate. (α.) If the ammonia be in *insufficient quantity* to neutralise the acid, a basic salt may be precipitated ($4CuSO_4 + 6H_3N + 7H_2O = 3(H_4N)_2SO_4 + CuSO_4,3CuO,4H_2O$); ($\beta$,) if it be added *in excess* a precipitate may be formed either of the hydrated metallic oxide, together with an ammonic salt ($2Fe_23SO_4 + 12H_3N + 9H_2O = 6(H_4N)_2SO_4 + 2Fe_2O_3,3H_2O$), or of a combination of ammonia with the precipitated oxide [as *e.g.*, uranic oxide, forming $(H_4N)_2O,2U_2O_3$], or of a double salt of the metal and ammonium, as *e.g.*, the ammonic-magnesic-phosphate $(H_4N)_2Mg_2P_2O_8,12H_2O$), or of various ammoniated salts, such as the ammoniated cupric sulphate, or of various substitution products where one or more atoms of hydrogen are replaced by a metal or by an electro-positive radical. Thus :—

Sodic amide (NH_2Na).
Ethylic amide, $NH_2(C_2H_5)$.
Acetamide $NH_2(C_2H_3O)$.

Solution of Ammonia (Liquor Ammoniæ, Spirits of Hartshorn).—This is a solution of the gas in water. Great heat is evolved during absorption.

At 32° F. 0° C. water absorbs 1050 vols. of NH_3.
At 59° F. 15° C. „ „ 727 „ „ „
At 77° F. 25° C. „ „ 586 „ „ „

The gas is evolved at ordinary temperatures. When these solutions are boiled, the whole of the ammonia is evolved. Nearly all the gas escapes by diffusion on exposing the solution to air, a quantity of heat being absorbed during its liberation equal to that which was given out during its formation.

The specific gravity of the solution of ammonia varies with its strength. (See Table IV. in Appendix.)

Ammonia solution is a colorless, alkaline liquid; it has a very caustic taste, and blisters the skin. The solution dissolves many salts (as $AgCl$) and oxides (CuO,ZnO,Ag_2O) that are insoluble in water.

If the solution be pure, it should on evaporation leave no residue.

The impurities of a solution of ammonia are—

(*a*.) *Carbonic acid.—Test:* White precipitate with lime water.

(*β*.) *Chlorine.—Test:* White precipitate on adding argentic nitrate to the solution neutralised with nitric acid.

(*γ*.) *Sulphuric Acid.—Test:* White precipitate on adding baric nitrate to a solution neutralised with nitric acid.

(*δ*.) *Lime.—Test:* White precipitate with ammonic oxalate.

(*ε*.) *Lead or copper* (derived from the apparatus, or from the solution having been kept in a glass bottle containing lead).—*Test:* Brown or black precipitate with sulphuretted hydrogen.

Estimation of Ammonia.—As ammonic platinic chloride ($2NH_4\,Cl$, $PtCl_4$). This double salt is almost insoluble in water and quite insoluble in alcohol or ether.

Ammonium (NH_4).

This compound monad radical (often written *Am*) has never been isolated. Its possible existence and metallic nature have been inferred by the close relationship of the ammonium salts to those of sodium and potassium, and also by the production of an amalgam having the metallic lustre of ordinary amalgams, under circumstances where its formation is theoretically possible. This amalgam rapidly decomposes into mercury, ammonia and hydrogen.

The amalgam may be prepared as follows:—

(1.) By placing a globule of mercury, connected with the negative pole of a battery, on a piece of moistened sal ammoniac (NH_4Cl) (placed on a piece of platinum foil) connected with the positive pole.

(2.) By pouring a little potassic or sodic amalgam into a saturated solution of sal-ammoniac; under these circumstances, the amalgam rapidly swells up, potassic or sodic chloride being formed at the same time.

Compound of Nitrogen, Hydrogen and Oxygen.

Hydroxylamine (NH_3O).

History.—Discovered by Lossen.

Preparation.—By the direct union of nascent hydrogen and nitric oxide ($2NO + 3H_2 = 2NH_3O$), or by the action of nascent hydrogen on nitric or nitrous acids ($HNO_3 + 3H_2 = NH_3O + 2H_2O$).

Properties.—It is only known in solution, which is very alkaline. It acts as a powerful reducing agent. On distillation ammonia is evolved.

COMPOUNDS OF HYDROGEN WITH PHOSPHORUS.

1.	*Gaseous phosphoretted hydrogen* ...	PH_3.
2.	*Liquid phosphoretted hydrogen* ...	PH_2 or P_2H_4.
3.	*Solid phosphoretted hydrogen...* ...	P_2H or P_4H_2 (?).

Gaseous Phosphoretted Hydrogen (PH_3).

Molecular weight, 34. *Molecular volume*, ☐☐. *Specific gravity*, 1·19.

Synonyms.—*Phosphine or Phosphamine* (from its analogy to ammonia); *Phosphorous Trihydride.*

History.—Discovered by Guigembre (1783), whilst distilling potash with spirit that had been used for anatomical preparations. It was afterwards studied by Davy (1812), who devised other methods for its preparation; also by Dumas, Rose, etc.

Natural History.—Evolved during the decomposition of phosphorised organic bodies (odor of fish).

Preparation.—(1.) By heating phosphorous or hypophosphorous acids:—

$$(\alpha.)\quad \underset{\text{Phosphorous acid}}{4H_3PO_3} = \underset{\text{Phosphoretted hydrogen}}{PH_3} + \underset{\text{Phosphoric acid.}}{3H_3PO_4.}$$

$$(\beta.)\quad \underset{\text{Hypophosphorous acid}}{2H_3PO_2} = \underset{\text{Phosphoretted hydrogen}}{PH_3} + \underset{\text{Phosphoric acid.}}{H_3PO_4.}$$

(2.) By boiling phosphorus in a strong solution of an alkali or of an alkaline earth:—

$$\underset{\substack{\text{Potassic}\\\text{hydrate}}}{3KHO} + \underset{\text{Phosphorus}}{P_4} + \underset{\text{Water}}{3H_2O} = \underset{\substack{\text{Sodic hypo-}\\\text{phosphite}}}{3KH_2PO_2} + \underset{\substack{\text{Phosphoretted}\\\text{hydrogen.}}}{PH_3.}$$

[N.B.—(α.) Free *hydrogen* is also evolved by the action of an excess of free alkali on the hypophosphite, a phosphate being formed as well as the liquid PH_2.

(β.) If alcohol be used instead of water the non-inflammable form is generated.]

(3.) By decomposing calcic phosphide (prepared by passing phosphorus vapor over red-hot lime) with water ($Ca_3P_2+6H_2O=2PH_3+3CaH_2O_2$).

(4.) By the action either of water or of potassic hydrate on phosphoric hydro-iodide ($PH_3.HI$):—

(α.) $PH_3.HI=HI+PH_3$.

(β.) $PH_3.HI+KHO=PH_3+KI+H_2O$.

[N.B.—This PH_3 is not inflammable.]

(5.) Possibly PH_3 is produced in very small quantities by the action of nascent hydrogen on phosphorus.

Properties.—(α.) *Sensible and physical.*—A colorless, stinking gas, specific gravity 1·19. It may be liquefied by pressure, and is decomposed by heat and electricity. Water absorbs from one-fourth to one-fiftieth of its volume, according to the temperature.

(β.) *Chemical.*—Its constitution may be determined by passing electric sparks through a known volume of the gas, using carbon electrodes for the purpose. It will be found that 2 volumes of PH_3 yield 3 volumes of hydrogen. From, say, the weight of 2 litres of PH_3, deduct the weight of 3 litres of H, the remainder will be the weight of $\frac{1}{2}$ litre of phosphorus vapour. In other words $\frac{1}{2}$ volume of phosphorus vapor combines with 3 volumes of hydrogen to form 2 volumes of PH_3.

Although in constitution PH_3 would appear to be analogous to ammonia, it has no alkaline reaction, but is, on the contrary, feebly acid to blue litmus. Nevertheless its relationship to ammonia is more than theoretical, as is shown by its combining with certain acids, such as hydriodic and hydrobromic acids, forming with them the crystalline compounds *phosphoric hydro-iodide* ($PH_3.HI$) and *phosphoric hydro-bromide* ($PH_3.HBr$). With hydrochloric acid, its union may also be effected by cold and pressure ($PH_3.HCl$). All of these compounds are decomposed by water. As ordinarily prepared, PH_3 is spontaneously inflammable; but this is not the case with the pure gas. This spontaneous inflammability depends on the presence of a trace of the vapor of *liquid* phosphoretted hydrogen (PH_2) one part of which in 500 of PH_3 is sufficient to confer this property upon it. (1.) *The pure non-inflammable gas may be rendered inflammable* (α,) by mixing it with a little PH_2 vapor; or (β,) by bubbling it through nitric acid containing nitrous acid in solution, $\frac{1}{10000}$th part of its bulk of nitrous anhydride being sufficient for this purpose; or (γ,) by its admixture with hydrogen, carbonic oxide, or other combustible gas. (2.) *The spontaneously inflammable gas may be rendered non-inflammable* (α,) by passing it over charcoal; or

(β,) by exposing it to sunlight, or (γ,) by passing it through hydrochloric acid; in which latter cases (β and γ) the liquid phosphoretted hydrogen is decomposed into solid and gaseous phosphoretted hydrogen ($5PH_2=P_2H+3PH_3$); or (δ,) by exposing the gas to a freezing mixture, whereby the vapor of the liquid phosphoretted hydrogen is condensed, or lastly (ϵ,) by mixing it with certain vapors, such as those of ether, turpentine, alcohol, etc. When the impure gas is ignited, it produces wreaths of white smoke, due to the formation of phosphoric anhydride. The gas burns in oxygen, yielding water and metaphosphoric acid (HPO_3), and explodes when mixed with oxygen. The haloids, sulphurous acid, and some of the metals decompose it ($PH_3+4Cl_2=PCl_5+3HCl$). With iodine, phosphoric hydro-iodide (phosphoric iodide) (PH_3HI) is formed ($2PH_3+3I=PH_3HI+2HI$). This body, which is a powerful reducing agent, may also be prepared with due precautions by the action of iodine on phosphorus in the presence of water. Phosphoretted hydrogen is decomposed when passed into most metallic solutions, phosphides of the metals being precipitated ($3CuSO_4+2PH_3=3H_2SO_4+P_2Cu_3$). In the case of gold and silver salts, the metals are reduced, phosphoric acid remaining in solution ($8AgNO_3+PH_3+4H_2O=H_3PO_4+8HNO_3+4Ag_2$).

Liquid Phosphoretted Hydrogen, $P_2H_4=66$.

Molecular volume, ☐☐.

Preparation.—By passing phosphoretted hydrogen, prepared by the action of water on calcic phosphide, through a freezing mixture.

Properties.—A light yellow liquid, boiling at 95° F. (32° C.), not solidifying at —4° F. (—20° C.), very inflammable, and decomposed by sunlight or by contact with hydrochloric acid into solid and gaseous phosphoretted hydrogen. It fires on exposure to air. The presence of this body in gaseous phosphoretted hydrogen confers upon it the property of spontaneous inflammability. (Thénard.)

Solid Phosphoretted Hydrogen, P_4H_2 (?) $=126$ (?).

Preparation.—By the action of sunlight or of hydrochloric acid on liquid phosphoretted hydrogen, or by the action of hydrochloric acid on calcic phosphide.

Properties.—A yellow solid, firing at 302° F. (150° C.), insoluble in water and in alcohol, but soluble in a solution of potassic hydrate, gaseous phosphoretted hydrogen being evolved.

There is some doubt as to the composition and constitution of this body.

COMPOUNDS OF HYDROGEN AND SULPHUR.

Sulphuretted hydrogen	H_2S.
Persulphuretted hydrogen	H_2S_2 (?).
Hyposulphurous hydrosulphate	H_2S_3.

Sulphuretted Hydrogen, H_2S.

Molecular weight, 34. *Molecular volume*, $\boxed{}\boxed{}$. *Relative weight*, 17. *Specific gravity*, (0·0693 × 17)1·178. 1 *litre weighs* (0·0896 × 17) 1·523 *grm. and* 100 *cubic inches* 36·43 *grains.*

Synonyms.—*Dihydric sulphide; Hepatic air; Hydrogen monosulphide; Sulphidic acid; Hydrosulphuric acid.*

History.—Discovered by Scheele (1777).

Natural History.—(*a.*) In the *mineral* kingdom, sulphuretted hydrogen is found in the gases issuing from volcanoes, and often to the extent of 25 per cent.

It is found in certain mineral *waters*, as, *e.g.*, in those of Harrogate, Aix-la-Chapelle, etc., and in sea-water near the mouths of rivers. The water on the west coast of Africa is stated to contain 6 cubic inches of sulphuretted hydrogen per gallon, the smell of the gas being recognisable 27 miles out at sea. In these cases the conditions necessary for its formation are the presence both of organic matter and of sulphates, the former being oxidized by the oxygen of the latter, until a sulphide is formed ($CaSO_4 - O_4 = CaS$). When this sulphide is acted on by the carbonic acid in the water, sulphuretted hydrogen is set free ($CaS + H_2O + CO_2 = CaCO_3 + H_2S$). The unpleasant taste of many aërated waters is due to their having been manufactured with water containing organic matter and sulphates, whereby a sulphide is formed, which is decomposed by the carbonic acid present in large excess.

Its presence in sewer-gas results from the putrefaction of organic matters containing sulphur, as well as the process already described. In the neighbourhood of sulphate of ammonia works, it may often be detected in the air; for in distilling coal (as well as in the destructive distillation of all organic matters containing sulphur) large quantities of the gas are generated, which, combining with the ammonia, collect in the ammoniacal liquor. Large quantities of H_2S are also evolved in the final part of the process of tar distillation. It may be worth noting here that if present in a room, it may be entirely removed by setting free a trace of chlorine.

(β.) In the *vegetable* kingdom it is unknown, whilst (γ) in the *animal* kingdom it is found in intestinal flatus.

Preparation.—(1.) By the *direct union* of hydrogen and sulphur; (*a.*) By heating together sulphur and hydrogen; or (β,) by passing hydrogen into boiling sulphur; or (γ,) by burning hydrogen in sulphur vapor or sulphur vapor in hydrogen; or (δ,) by pouring boiling sulphur into water, or by passing steam and sulphur vapor through a tube filled with red-hot pumice-stone, SO_2 and H_2S being formed ($2H_2O + 3S = 2H_2S + SO_2$). The SO_2 and H_2S, in the presence of moisture, effect mutual decomposition ($10SO_2 + 10H_2S = 8H_2O + 2H_2S_5O_6 + 5S_2$).

(2.) By decomposing a metallic sulphide with an acid; *e.g.* :—

(α.) Dilute sulphuric acid on ferrous sulphide. (In this case the products usually contain a little free hydrogen from the presence of metallic iron in the sulphide)—

$$H_2SO_4 + FeS = FeSO_4 + H_2S.$$

Sulphuric acid + Ferrous sulphide = Ferrous sulphate + Sulphuretted hydrogen.

(β.) Dilute hydrochloric acid on antimonious sulphide. (In this case the products are free from hydrogen)—

$$6HCl + Sb_2S_3 = 2SbCl_3 + 3H_2S.$$

Hydrochloric acid + Antimonious sulphide = Antimonious chloride + Sulphuretted hydrogen.

(3.) By heating sulphur in the presence of certain organic bodies (as paraffin).

(4.) By the putrefactive decomposition of organic bodies containing sulphur.

Properties.—(α.) *Sensible and physiological.* Sulphuretted hydrogen is a colorless gas, having the odor of rotten eggs. Physiologically, it acts as a narcotic and is very poisonous; 1 part in 1,500 will kill birds; 1 in 1,000, dogs; 1 in 250, horses. (Dupuytren and Thénard.)

(β.) *Physical.* Its specific gravity is 1·178. 100 cubic inches weigh 36·43 grains, and 1 litre 1·523 grms. By a pressure of seventeen atmospheres at 50° F. (10° C.), or by a cold of —101° F. (—74° C.), it may be condensed into a colorless liquid, which boils at —79·6° F. (—62° C.), and freezes at —122·8° F. (—86° C.). It is decomposed by a heat of 752° F. (400° C.). Water freely absorbs it. At 32° F. (0° C.) it dissolves 4·37 times its bulk of the gas; at 59° F. (15° C.), 3·23 volumes, and at 75° F. (24° C.) 2·66 volumes. The gas is evolved from its solution on boiling, and is oxidised with separation of sulphur by keeping.

(γ.) *Chemical.* Its composition may be determined by heating a known volume of the gas with metallic tin or other metal that combines with the sulphur. It will be found that the liberated hydrogen occupies the same volume as the original gas.

Sulphuretted hydrogen reddens litmus feebly. It is a combustible gas. If the supply of air be free, water, sulphurous acid, together with a little sulphuric acid if the air be moist, are formed. If the supply of air be limited, sulphur will be deposited. It will be noted, therefore, that any sulphuretted hydrogen evolved during manufacturing operations should theoretically be removed by passing the gas through the furnace.

Mixed with *oxygen* in the proportion of 1 volume of H_2S to 1·5 of O, it explodes on the application of heat. By the action of chlorine, bromine, and iodine, sulphuretted hydrogen is immediately decomposed, the haloid element appropriating the hydrogen, sulphur being liberated ($SH_2+Cl_2=2HCl+S$). With chlorine and bromine this action takes place without the presence of moisture, but in the case of iodine moisture is essential. *Oxy-acids* (such as nitric, sulphuric, etc.) decompose it, setting free sulphur ($H_2SO_4 + H_2S = SO_2 + 2H_2O+S$). With fuming nitric acid, oxidation results with explosive violence. It is absorbed by the *alkalies*, forming sulphides (as K_2S), solutions of which, on being further treated with sulphuretted hydrogen, form sulphydrates (hydrosulphides) ($K_2S+H_2S=2KHS$). (Action of SO_2, *see* pages 179 and 267.)

Certain *metals* decompose the gas, displacing hydrogen, a metallic sulphide being formed. This occurs in some cases at *ordinary temperatures* (as *e.g.*, in the case of Hg, Ag, etc.), ($Hg_2+H_2S=Hg_2S+H_2$). Thus, silver is blackened by exposure to the air of towns, a silver spoon by the sulphur of an egg, and silver coins by being kept with sulphur matches in the pocket. [The black sulphide thus formed may be removed by strong ammonia or by potassic cyanide.] In other cases, *heat* is required to effect combination (as *e.g.*, with K, Sn, etc.):—

(α.) $2H_2S+K_2=2KHS+H_2$. (β.) $H_2S+Sn=SnS+H_2$.

In this latter case it will be remarked that the volume of hydrogen evolved is identical with the volume of sulphuretted hydrogen operated upon. *Metallic oxides* are changed by the action of the gas into their corresponding sulphides, the sulphuretted hydrogen being decomposed and water formed ($PbO+H_2S=PbS+H_2O$). A similar action is observed in the case of the metallic salts ($Pb(NO_3)_2+H_2S=2HNO_3+PbS$). Thus, the lead used for paint becomes black, although the black sulphide (PbS) formed is, under the influence of air and light, converted into the white sulphate ($PbSO_4$). The colors of the various sulphides produced when the gas is passed through metallic solutions are, in many cases, very characteristic, and constitute important tests. Some are soluble in water: others are soluble in weak acids, but insoluble in alkaline solutions; others again are insoluble in weak acids. Thus we differentiate the sulphides:—

Metallic Sulphide.	*Metals.*
(1.) Insoluble in weak acids	Precipitated by H_2S in acid solution of salts.
(2.) Soluble in weak acids, but insoluble in alkalies	Precipitated by an alkaline sulphide, or by H_2S in neutral or alkaline solution.
(3.) Soluble in water	Not precipitated by H_2S either in an acid or alkaline solution.

On *metallic chlorides* the action of the gas is similar to that on the oxides.

The solution of sulphuretted hydrogen has a feebly acid reaction. It rapidly decomposes and becomes turbid, from atmospheric oxygen combining with the hydrogen, whereby sulphur (the electro-negative variety) is precipitated as a white deposit. It is better, therefore, to make the solution with a water either that has been well boiled, or has been previously saturated with the gas.

Uses.—In the laboratory, as a test for the metals.

Tests.—Blackens lead paper.

Persulphuretted Hydrogen (H_2S_2 (?)).

Molecular weight 66 (?). *Specific gravity*, 1·769.

Synonyms.—*Persulphide of hydrogen; Hydric persulphide; Dihydric disulphide; Hydrosulphyl* (Frankland).

History.—Discovered by Scheele (1777). Its properties were fully investigated by Berthollet.

Preparation.—Lime and milk of sulphur are first boiled together, whereby a disulphide of calcium is formed (CaS_2). This solution is then dropped into dilute hydrochloric acid (1 of acid to 2 of water):—

$$\underset{\text{Calcic disulphide}}{CaS_2} + \underset{\text{Hydrochloric acid}}{2HCl} = \underset{\text{Persulphuretted hydrogen}}{H_2S_2} + \underset{\text{Calcic chloride}}{CaCl_2}.$$

[NOTE.—Persulphuretted hydrogen is more stable in contact with acids than with alkalies. Hence, if the acid be poured into the calcic disulphide solution, a different reaction results from that given above, sulphur being precipitated (sulphur præcipitata, P.B.) $CaS_2 + 2HCl = CaCl_2 + H_2S + S$.]

Properties.—(*a.*) *Sensible and physiological.*—A yellowish oily liquid having a sulphuretted hydrogen odor. Specific gravity, 1·769. It is a very unstable body, undergoing decomposition by slight heat into sulphuretted hydrogen and sulphur. It is neither soluble in water, chloroform, nor benzol, but is soluble in ether and bisulphide of carbon.

(*β.*) *Chemical.*—Persulphuretted hydrogen is inflammable, and burns with a blue flame. Some question exists as to its precise composition, later researches indicating H_2S_3 as a more probable formula (see below). It is, however, generally regarded as a sulphide of hydrogen (H_2S_2) analogous to hydroxyl (H_2O_2). Further it is closely allied to H_2O_2 in certain of its reactions. Thus, it bleaches litmus. The presence of acids increase, whilst alkalies decrease its stability. It dissolves free sulphur, and is decomposed, like hydroxyl, by the mere contact of certain metals and metallic peroxides. (Odling.) It is believed to combine with many vegetable alkaloids. It differs from sulphuretted hydrogen, in that sulphurous acid is without action upon it.

Hyposulphurous Hydrosulphate (H_2S_3).

Preparation.—By the action of sulphuric acid and afterwards of water on the compound formed when an alcoholic solution of yellow ammonic sulphide is added to a cold alcoholic solution of strychnia. (See above.)

Seleniuretted Hydrogen (H_2Se).

Molecular weight, 81·5. *Molecular volume*, □□. *Specific gravity*, 2·8.

Synonyms.—*Selenetted hydrogen; Hydroselenic acid; Dihydric selenide; Selenhydric acid.*

History.—Discovered by Berzelius.

Preparation.—(1.) By passing hydrogen and selenium vapor through red-hot tubes.

(2.) By the action of acids on selenides :—

$FeSe$	+	$2HCl$	=	H_2Se	+	$FeCl_2$.
Ferrous selenide	+	Hydrochloric acid	=	Seleniuretted hydrogen	+	Ferrous chloride.

Properties.—(*a.*) *Sensible, physical, and physiological.*—A colorless, offensive-smelling gas, producing great irritation and violent nasal catarrh. It is decomposed by heat into selenium and hydrogen, decomposition beginning at 302° F. (150° C.), the intensity of action increasing to 518° F. (270° C.). From this point it decreases until 968° F. (520° C.) is reached, when the action ceases, re-commencing at a still higher temperature. Specific gravity, 2·8. Soluble in water.

(*β.*) *Chemical.* Burns in air, yielding SeO_2 and H_2O. Its solution in water is feebly acid. When exposed to the air it absorbs oxygen, depositing selenium. Its reactions are closely allied to those of sulphuretted hydrogen, precipitating in many cases metallic selenides when passed through solutions of metallic salts. The alkaline selenides are soluble. The selenides of zinc and manganese are colored, but the rest are black.

Telluretted Hydrogen ($H_2Te=127$).

Preparation.—By the action of dilute hydrochloric acid on zinc or on other tellurides ($ZnTe+2HCl = H_2Te + ZnCl_2$).

Properties.—A colorless, fœtid gas. The action of heat upon it is similar to that upon seleniuretted hydrogen (*q. v.*). It burns in air, yielding TeO_2 and H_2O.

COMPOUNDS OF CARBON AND HYDROGEN.

These compounds, generically termed hydrocarbons, belong chiefly, if not entirely, to organic chemistry. Three of these compounds will be described here, viz., marsh gas, CH_4, olefiant gas, C_2H_4, and acetylene, C_2H_2. These three bodies are, moreover, the starting-points of three series of hydrocarbons, the members of which, as in the case of other hydrocarbon series, increase by a regular increment of, or some multiple of CH_2, such series being termed an *homologous series.* Thus—

Marsh Gas Series.	*Olefiant Gas Series.*	*Acetylene Series.*
$(CH_2)_n + H_2$.	$(CH_2)_n$.	$(CH_2)_n - H_2$.
Methane (marsh gas) CH_4	Ethylene (olef. gas) C_2H_4	Acetylene .. .. C_2H_2
Ethane .. .. .. C_2H_6	Propylene .. .. C_3H_6	Allylene .. .. C_3H_4
Propane .. .. .. C_3H_8	Butylene .. .. C_4H_8	Crotonylene .. C_4H_6
Etc.	Etc.	Etc.

Methane, or Light Carburetted Hydrogen, CH_4.

Molecular weight, 16. *Molecular volume,* ☐☐. *Specific gravity, observed* 0·5576; *estimated* (0·0693 × 8) 0·554. 1 *litre weighs* (0·0896 *grm.* × 8) 0·7168 *grm., and* 100 *cubic inches,* 17·144 *grains.*

Synonyms.—*Marsh gas; Methane; Methylic hydride* (CH_3H); *Sub-carburetted hydrogen; Heavy inflammable air; Fire damp; Pit gas.*

History.—First examined by Volta (1778).

Natural History.—Found in stagnant ditches, *i. e.*, wherever vegetable matter is decomposing out of contact with air, but in the presence of moisture (hence termed "marsh gas"). It occurs occluded in coal, 100 grains of which will at times yield 200 c.c. of a gas containing nearly 90 per cent. of marsh gas, the remaining 10 per cent. consisting of nitrogen, oxygen, and carbonic acid. It is also found occluded in meteorites (Dewar and Ansdell), and is evolved from the earth in many volcanic districts.

Preparation.—(1.) By the decomposition of moist organic matter out of contact with air.

(2.) By the dry distillation of coal.

[Probably CH_4 and CO_2 were the two gases formed when the hydrogen and oxygen were separated from the wood during conversion into coal.]

(3.) By heating acetic acid or an acetate, with sodic or potassic hydrate :—

$KC_2H_3O_2$	+	KHO	=	K_2CO_3	+	CH_4
Potassic acetate	+	Potassic hydrate	=	Potassic carbonate	+	Methane.

(4.) By passing a mixture of carbonic disulphide vapor with either (*α*) sulphuretted hydrogen, or (*β*) steam over red-hot copper :—

(*α*.)	CS_2	+	$2H_2S$	+	$4Cu$	=	$4CuS$	+	CH_4.
	Carbonic disulphide	+	Sulphuretted hydrogen	+	Copper	=	Cupric sulphide	+	Methane.

(*β*.)	CS_2	+	$2H_2O$	+	$6Cu$	=	CH_4	+	$2Cu_2S$	+	$2CuO$.
	Carbon disulphide	+	Water	+	Copper	=	Methane	+	Cuprous sulphide	+	Oxide of copper.

(5.) By the action of water on zinc methide :—

$Zn(CH_3)_2$	+	$2H_2O$	=	$2CH_4$	+	ZnO_2H_2.
Zinc methide	+	Water	=	Methane	+	Zincic hydrate.

(6.) By the action of nascent hydrogen on chloroform ($CHCl_3$), or on chloride of carbon (CCl_4), or on iodoform (CHI_3), etc. :—

$$CHCl_3 \quad + \quad 3H_2 \quad = \quad CH_4 \quad + \quad 3HCl.$$

Chloroform + Hydrogen = Methane + Hydrochloric acid.

Properties.—(a.) *Sensible and physiological.*—A colorless, odorless, tasteless gas. It has no injurious or toxic action on the body.

(β.) *Physical.*—Specific gravity, 0·5576. It possesses great powers of diffusion. It may, although with difficulty, be completely decomposed by heat and electricity, carbon being deposited, the volume of hydrogen evolved being double the volume of the original gas. (Page 42). Passed through a red-hot tube, hydrogen, ethylene, acetylene, and ethylic hydride are formed. 100 volumes of water at 32° F. (0° C.) absorb about 5·4 volumes of the gas.

(γ.) *Chemical.*—CH_4 is a very inert gas, and constitutes the first member of the *paraffin* series (*parum* and *affinitatis*). It has no action on turmeric or litmus. It contains more hydrogen than any other compound of carbon and hydrogen. It burns with a pale illuminating flame, a white heat or actual flame being required for its ignition, carbonic anhydride and water constituting, if the supply of air be free, the products of its combustion, acetylene and other bodies being formed if the supply be limited. Exploded with *twice* its volume of oxygen, carbonic anhydride and water result, whilst when the volume of oxygen is one and a-half times that of the methane, carbonic oxide and water are formed. It explodes even when mixed in the proportion of 1 volume of methane to 17 of air, the energy of the explosion increasing until the methane constitutes one-seventh part of the total volume.

Action of the Haloids.—Iodine and bromine, are without action upon CH_4. Chlorine does not combine with it in the dark, whilst in sunlight union is intensely energetic, forming, in the presence of moisture, carbonic anhydride and hydrochloric acid ($CH_4 + 4Cl_2 + 2H_2O = CO_2 + 8HCl$). If the chlorine be present in great excess, substitution of chlorine for the hydrogen may be effected, carbon tetrachloride, CCl_4, or such lower derivatives such as $CHCl_3$, etc., being formed.

Neither sulphur, phosphorus, acids nor alkalies, have any action upon it.

Ethylene or Heavy Carburetted Hydrogen, C_2H_4.

Molecular weight, 28. *Molecular volume*, ☐☐. *Specific gravity, observed* 0·978; *estimated* (0·0693 × 14) 0·9702. 1 *litre weighs* (0·0896 *grm.* × 14) 1·254 *grm.*, *and* 100 *cubic inches*, 30·00 *grains.*

Synonyms.—*Olefiant gas* (Dutch chemists); *Ethylene*; *Elayl* (Berzelius); *Etherene* (Faraday); *Etherin.*

History.—Discovered by the Associated Dutch Chemists (1795). Afterwards studied by Berthollet.

Natural History.—Present to the extent of 1 to 6 per cent. in fire-damp.

Preparation.—(1.) By the dry distillation of coal and other organic bodies (resins, fats, oils, etc.).

(2.) By the action of sulphuric acid (or other dehydrating agents, such as boric anhydride) on alcohol at a temperature of about 329° F. (165° C.). This action occurs in two stages :—

(*a.*) Sulphovinic acid is first formed—

$$C_2H_5(HO) + H_2SO_4 = (C_2H_5)HSO_4 + H_2O.$$

Alcohol + Sulphuric acid = Sulphovinic acid + Water.

(*β.*) The sulphovinic acid is afterwards decomposed by heat into ethylene and sulphuric acid—

$$(C_2H_5)HSO_4 = C_2H_4 + H_2SO_4.$$

Sulphovinic acid = Ethylene + Sulphuric acid.

(3.) By the action of nascent hydrogen on acetylene ($C_2H_2+H_2=C_2H_4$).

[Note.—Acetylene, C_2H_2, is the only hydrocarbon that can be prepared directly from its elements. From it ethylene, and from ethylene, alcohol may be formed.]

(4.) By the action of an alcoholic solution of potassic hydrate on ethyl chloride, bromide, or iodide :—

$$C_2H_5Br + KHO = C_2H_4 + KBr + H_2O.$$

Ethyl bromide + Potassic hydrate = Ethylene + Potassic bromide + Water.

Properties.—(*a.*) *Sensible.* A colorless, odorless gas, having an anæsthetic action.

(*β.*) *Physical.* Specific gravity 0·978. It may be liquefied by cold and pressure at —166° F. (—110° C.) (Faraday). It is decomposed by a red heat and by electric sparks. If the heat be not too great, acetylene and hydrogen are formed ($C_2H_4 = C_2H_2 + H_2$) ; at a higher temperature marsh gas is produced, and one-half of the carbon is deposited ($C_2H_4 = CH_4 + C$), whilst at a still higher temperature it undergoes complete decomposition ($C_2H_4 = C_2 + 2H_2$). Water absorbs about one-eighth its bulk of the gas. Alcohol, ether, the volatile and fixed oils dissolve it.

(*γ.*) *Chemical.* It has no action either on litmus or turmeric. It burns with an intensely white light, and constitutes one of the chief illuminants of coal gas. When mixed with three volumes of oxygen, it explodes ($C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$), water and carbonic anhydride resulting.

Its most striking chemical property is its power to combine directly with other substances, particularly with the haloid elements and their hydrogen acids.

Action of the Haloids.—(*a.*) When olefiant gas is fired with twice its volume of chlorine, it deposits carbon, hydrochloric acid being formed. (*β.*) Mixed with its own volume of chlorine and exposed to diffuse light, it forms an oily fluid called *Dutch liquid*, $C_2H_4Cl_2$ (Dichlorethane ; Ethylene chloride). This liquid has a specific gravity of 1·256 at 53·6° F. (12° C.), and boils at 183·2° F. (84° C.). The fact of the formation of this body gives the name "Olefiant Gas." (γ.) When the gas is mixed with a larger proportion of chlorine, and exposed to sunlight, the product C_2Cl_6 may be formed. Bromine, but not iodine, forms products of a similar kind. An *Ethylene iodide*, $C_2H_4I_2$ may be produced by passing ethylene into a mixture of iodine and absolute alcohol.

Phosphorus and sulphur have no action upon it.

Fuming sulphuric acid, or sulphuric anhydride, absorbs it, forming $C_2H_4,2SO_3$ (ethyl-sulphuric acid). Mixed with an alkaline solution of potassic permanganate, carbonic, formic, and oxalic acids are produced.

Acetylene, C_2H_2.

Molecular weight, 26. *Molecular volume*, □□. *Specific gravity observed*, 0·92 ; *estimated*, 0·900. 1 *litre weighs* (0·0896 *grm.* × 13) 1·164 *grm. and* 100 *cubic inches* 27·859 *grains.*

Synonyms.—*Ethine ; Klumene.*

Preparation.—(1.) By the direct combination of carbon with hydrogen ; as, *e.g.*, by the combustion of the carbon poles from a powerful battery in an atmosphere of hydrogen.

(2.) By the incomplete combustion of bodies containing carbon and hydrogen, such *e.g.*, as methane, vapor of alcohol, etc., by passing them through a tube heated to redness. Also by burning coal gas in an insufficient supply of air, etc.

(3.) By the action of an alcoholic solution of potassic hydrate on ethylene bromide (bromethylene) :—

C_2H_3Br	+	KHO	=	C_2H_2	+	KBr	+	H_2O.
Bromethylene	+	Potassic hydrate	=	Acetylene	+	Potassic bromide.	+	Water.

(4.) By the electrolysis of fumaric acid ($C_2H_2(COOH)_2 = C_2H_2 + 2CO_2 + H_2$).

(5.) By passing a mixture of methane and carbonic oxide through a red-hot tube ($CH_4 + CO = C_2H_2 + H_2O$).

Properties.—(*a.*) *Sensible.* A colorless gas, having a geranium odor. It is very poisonous.

(β.) *Physical.* Specific gravity 0·92. It is decomposed by an intense heat (such as electric sparks) with the separation of carbon. By the action upon it of a continuous red heat, benzene (C_6H_6) has been formed, together with a liquid hydro-carbon called styrole (C_8H_8), which hitherto had only been obtained from storax. Acetylene is the most stable of all carbon compounds. It is soluble in water, the solution answering to the tests.

(γ.) *Chemical.*—It burns with a smoky flame, 1 volume of gas consuming 2·5 volumes of oxygen, and forming 2 volumes of CO_2. Mixed with chlorine and exposed to diffuse daylight, it explodes spontaneously, with the separation of carbon ($C_2H_2 + Cl_2 = C_2 + 2HCl$). It combines with bromine to form acetylene dibromide or tetra-bromide ($C_2H_2Br_2$, and $C_2H_2Br_4$). It unites with hydriodic and hydrobromic acids, forming substitution products of the saturated hydrocarbons ($C_2H_2 + 2HI = C_2H_4I_2$). When electric sparks are passed through a mixture of nitrogen and acetylene, hydrocyanic acid is formed ($C_2H_2 + N_2 = 2CHN$). Oxidizing agents, such as potassic permanganate, convert it into oxalic acid. It is absorbed by sulphuric acid, with the production of vinyl-sulphuric acid (C_2H_2,H_2SO_4). It combines directly with nascent hydrogen to form olefiant gas ($C_2H_2 + H_2 = C_2H_4$).

Tests.—(*a.*) With *cuprous chloride* acetylene forms hydrochloric acid and a red explosive precipitate of cuproso-vinyl oxide [cuprous acetylide or cuproso-vinylic ether], ($2Cu_2Cl_2 + 2C_2H_2 + H_2O = 4HCl + C_2H_2,Cu_2O$). This body is supposed to have caused explosions in brass and copper pipes used for gas, as it explodes when dry at 248° F. (120° C.). It is immediately decomposed by hydrochloric acid, acetylene being set free ($C_2H_2,Cu_2O + 4HCl = 2Cu_2Cl_2 + H_2O + 2C_2H_2$).

(*β.*) Acetylene gives a white explosive precipitate with argentic nitrate, insoluble in ammonia or in nitric acid.

Coal Gas.

Three classes of products are formed by the dry distillation of coal—gas, water, and tar, the relative proportions of each depending much on the temperature to which the coal is subjected. Coal gas is a compound gas, consisting of illuminants, diluents and impurities. The *illuminants* are olefiant gas (C_2H_4), analogous hydrocarbons (C_3H_6, C_4H_8, etc.), and hydrocarbon vapors, such as the vapor of benzol. The *diluents* are hydrogen, marsh gas, and carbonic oxide. The *impurities* are carbonic anhydride, sulphuretted hydrogen, and other sulphur compounds.

The following table from Roscoe, represents the composition of coal gas, prepared respectively from cannel and from common coal. In estimating the illuminating power of a gas, we compare the light given by the gas burning from a 24-hole argand, at 5 feet per hour, with a sperm candle burning at the rate of 120 grains.

	Illuminating power compared to sperm candle burning 120 grains per hour, the gas burning 5 cubic feet.	Composition in 100 volumes.					
		Hydrogen, H.	Marsh gas, CH_4.	Carbonic oxide, CO.	Heavy Hydrocarbons $(CH_2)n$.	Equal to Olefiant gas, C_2H_4.	Nitrogen, Oxygen, and Carbonic acid.
Cannel gas	34·4	25·82	51·20	7·85	13·06	(22·08)	2·07
Coal gas	13·0	47·60	41·53	7.82	3·05	(6·97)	—

The gas is purified by condensation and by absorption.

(1.) By *condensation* (refrigerators) the solid and liquid impurities, such as naphthalene, water, tar, etc., are removed.

(2.) By *absorption* (lime and oxide of iron purifiers). By the former, the carbonic acid, the presence of 1 per cent. of which is said to decrease the light 6 per cent., is removed; and by the latter, the sulphur present as sulphuretted hydrogen, and to a certain extent in other forms.

Flame.

Flame results from the combination of two gases under the influence of heat. A gas to burn, therefore, is one essential condition of flame. Hence a diamond cannot burn with flame, because it cannot be volatilized. Further it is essential that the temperature necessary to effect the union of the gases concerned in the action should be maintained. Hence, a mass of cold metal introduced into a flame may be made to extinguish it.

The terms "*combustible*" and "*supporter of combustion*" are, however, merely conventional, inasmuch as air may be made to burn in coal gas.

The temperature at which this combination of different gases (*i. e.*, combustion) occurs, varies with different gases. Thus, *phosphoretted hydrogen* ignites at ordinary temperatures, *carbon disulphide* vapor at 419° F. (215° C.), whilst marsh gas needs a temperature little short of actual flame to effect ignition.

Combustion may proceed both (α) *without flame*, as instanced by a smouldering taper, or by the action of a hot platinum wire on mixed air and coal gas; and (β) *with flame*, as in the ordinary cases of combustion.

The products of the quick and slow combustion of the same body vary. The *rapid* combustion of alcohol (C_2H_5HO) yields H_2O and CO_2; whilst its *slow* combustion yields aldehyde (C_2H_4O).

An ordinary flame burning in air, is an envelope dividing the combustible gas within the flame from the supporter of the combustion without. It consists of several parts :—

(1.) A dark inner cone of unburnt gas. This is surrounded by—

(2.) A luminous cone of partly burnt gas. It is in this cone that the carbon is separated and dense hydrocarbons formed. This occurs as follows :—The air present is insufficient to burn both the hydrogen and the carbon of the hydrocarbon; consequently, the hydrogen having a greater affinity for oxygen than the carbon, combines with it, and the carbon is set free, which, becoming ignited and incandescent in the burning hydrogen, renders the flame luminous. This luminous cone is surrounded by—

(3.) A non-luminous, but intensely hot cone of completely-burnt gas.

(4.) At the bottom part of the flame is a portion where the combustion is complete. At this point the division into the cones described, is not apparent.

In a *blow-pipe* flame a free supply of air is effected within the flame. Thus, the carbon of the hydrocarbon is burnt as well as the hydrogen. A blow-pipe flame consists of two parts, each part having a different chemical power. (*a.*) *The point of the inner cone* has a *reducing action,* due to the presence of an *excess of carbon* in the form of carbonic oxide, which is ready to combine with more oxygen. (*β.*) *The point of the outer cone* has an *oxidizing action*, due to the presence of an *excess of oxygen.*

The heat of a flame depends on the energy of the chemical combination. Thus it bears no necessary relationship to the light emitted by the flame. The oxy-hydrogen jet is non-luminous but enormously hot, the energy of the chemical action being intense. If lime be introduced into the jet the light becomes intense, but the heat produced is lessened, inasmuch as the lime not only does not contribute to the chemical action, but conducts the heat away.

The light of a flame depends on several circumstances. (*a.*) In most cases, but not necessarily as Frankland has shown, light depends *on solid, incandescent particles.* Thus, when solid particles are introduced into the colorless flame of hydrogen it is rendered luminous. We may, however, have a luminous flame without solid particles. A bright light is produced, for example, when metallic arsenic is burnt in oxygen, although both the metal and the product of its combustion are gaseous at the temperature of the flame. A mixture of nitrogen dioxide and carbon disulphide again, burns with a luminous flame. (*β.*) *Temperature.* Thus sulphur, phosphorus, and other bodies give more light when burnt in oxygen than in air, the nitrogen of the air in such cases not only contributing nothing to the energy of the combustion, but lowering the temperature, by the removal of the heat resulting from the combination of the burning body with oxygen. (*γ.*) *Density of the gases.* This may be considered from two points of view:—(1.) *The density of the gas supporting combustion.* An alcohol flame burns with a very feeble light in air at 30 inches Bar. Pr., but the combustion is accompanied by considerable luminosity in an atmosphere at 120 inches Bar. Pr. A candle gives less light on the top of a mountain than in the valley, although the tallow may be consumed at the same rate in each. Thus *increased* light results from *condensing,* and *decreased* light from *rarefying* the surrounding atmosphere. (2.) *The density of the combustible gas and of the products of the combustion.* It would appear that luminosity is closely related to the vapor density of the products, the higher the specific gravity of the products, the more intense the light. Thus, *e.g.*, when hydrogen is burnt in *air*, it produces water, which has a density of 9; whilst if burnt in *chlorine,* it forms hydrochloric acid, which has a density of 18·25. Hence, the light produced by burning hydrogen in chlorine, is much greater than that produced by burning hydrogen in air. Sulphur burnt in oxygen forms SO_2 (density 32)—phosphorus when burnt in oxygen forms P_2O_5 (density 142); hence the greater light given by phosphorus over sulphur.

The color of a flame depends upon the kind of solid particles present. Thus sodium renders a flame yellow, and lithium red. Further there are cases where the temperature of the gas before combustion affects the color of the flame. This happens with carbonic oxide, the cold gas giving a blue, and the hot gas a yellowish-red flame.

We may here note that to obtain a maximum light from any flame :—

(1.) *The supply of air must not be excessive*, otherwise combustion will be too complete, the luminosity of the flame being decreased for two reasons, (α) that the carbon particles are consumed before they are sufficiently heated to emit light, and (β) that the excess of atmospheric nitrogen serves to cool the flame, thereby decreasing its illuminating power. This is illustrated by blowing on a flame, or by the increase of draught effected by lengthening the chimney.

(2.) *The supply of air must not be too limited*, otherwise the carbon passes off unburnt. The flame thus becomes smoky.

COMPOUND OF HYDROGEN AND SILICON.

Silicic Hydride (SiH_4=32).

Synonym.—*Hydride of Silicon; Siliciuretted Hydrogen.*

Preparation.—(1.) By decomposing magnesic silicide (prepared by heating together magnesic chloride, sodic silico-fluoride, fused sodic chloride and metallic sodium) with dilute hydrochloric acid. (Wöhler.)

(2.) By passing a galvanic current through a sodic chloride solution, the positive pole being composed of aluminium containing silicon.

Properties.—A colorless gas. When impure it fires spontaneously in air, giving off white fumes of amorphous silica. The pure gas does not ignite spontaneously. Burnt in oxygen it yields water and silica. It explodes with chlorine, forming $SiCl_4$ and HCl. It is decomposed by heat into amorphous silicon and free hydrogen, the hydrogen occupying twice the volume of the original gas. With potassic hydrate it undergoes decomposition, yielding potassic silicate and four times its volume of free hydrogen ($SiH_4 + 2KHO + H_2O = K_2SiO_3 + 4H_2$). It precipitates many metallic solutions, but not those of lead or of platinum ($2CuSO_4 + SiH_4 = Cu_2Si + 2H_2SO_4$).

Silicic Hydrotrichloride.—($SiHCl_3$) (*Silicon Chloroform*), is prepared by heating crystallized silicon in a stream of hydrochloric acid ($Si + 3HCl = SiHCl_3 + H_2$). It is a fuming liquid, boiling at 96·5° F. (36° C.). The vapor is very inflammable, and explodes when mixed with oxygen. It is decomposed (1) by passing it through a red-hot tube, or (2), at ordinary temperatures by the action of chlorine, or (3), by contact with water.

Silico Formic Acid, or **Leukon** (λευκὸς, white), (SiH_2O_2), *silicon formanhydride*). (*See* page 226.)

Silicic Iodoform ($SiHI_3$), corresponding to silicon chloroform, has been prepared by passing hydrogen and hydriodic acid over heated silicon. It is a liquid (Sp. Gr. 3·362), and is decomposed by water.

Hydrofluosilicic Acid (H_2SiF_6). *See* page 257.

Boric Hydride (BH_3(?))

Preparation.—A magnesic boride is formed by heating together magnesium and boric anhydride. Boric hydride is evolved by the action of hydrochloric acid on magnesic boride. (F. Jones.)

B_2Mg_3	+	$6HCl$	=	$2BH_3$	+	$3MgCl_2$.
Magnesic bromide	+	Hydrochloric acid	=	Boric hydride	+	Magnesic chloride.

Properties.—A colorless, offensive gas, sparingly soluble in water. It burns with a blue flame, yielding boron or boric anhydride, accordingly as the supply of air be limited or free. It is decomposed by heat. With a solution of nitrate of silver it yields a black precipitate containing boron and silver.

SECTION II.—THE METALS.

CHAPTER XI.

GENERAL REMARKS ON THE METALS.

Derivation and Definition of a Metal — Order of Discovery — Natural History — Physical and Sensible Properties—Chemical Properties—Classification of the Metals.

Derivation.—Μέταλλον a metal. The word is found in every modern language.

Definition.—Our definition of a metal is twofold. *Physically*, "it is an opaque body, having a metallic lustre, and possessing for the most part a good conducting power for heat and electricity." *Chemically*, "it is an element capable of forming a base by its combination with oxygen, and a salt by its combination with a salt radical."

The division, however, of inorganic bodies into metals and non-metals, or as they were often called, metalloids, is, strictly speaking, one of convenience only.

Order of Discovery.—Seven metals were known to the ancients (viz., Au, Ag, Cu, Pb, Fe, Hg, Sn,) ; one was discovered in the fifteenth century (viz., Sb) ; two in the sixteenth (viz., Bi and Zn) ; eleven in the eighteenth (viz., As, Cr, Co, Mn, Mo, Ni, Pt, Te, Ti, W, U) ; and the rest in the nineteenth.

Natural History. - (α.) In the *mineral* kingdom, the metals are found (1) native, either in a free state (as gold, silver, etc.), or as alloys (as *e.g.*, gold with silver, gold with palladium, etc.) ; or (2) in combination with sulphur (as galena, PbS), with oxygen (as hæmatite, Fe_2O_3), or with the haloids (as common salt, $NaCl$); or (3) as oxy-salts, as *e.g.*, sulphates (heavy spar, $BaSO_4$), carbonates (strontianite, $SrCO_3$), phosphates (apatite), etc. (β.) In the *vegetable kingdom*, sodium and potassium are found in all plants, and manganese, silver and lithium in most. (γ.) In the *animal kingdom*, iron is found in the blood, manganese in the hair, calcium in the bones, etc.

As regards *distribution*, some are widely distributed over the whole crust of the earth (*e.g.*, Ca, Al, Mg, Na, Fe), whilst others are found in small quantities, and in few localities only. Usually, they occur in cracks (lodes) in particular rocks (as *e.g.*, Au, Ag, etc.), whilst in other cases they are found as ores, such as ironstone, in the more recent sedimentary formations.

I. Sensible and Physical Properties.—(1.) *Color.* This varies as follows :—(*α.*) Red (Cu) ; (*β.*) Bright yellow (Au) ; (*γ.*) Pale yellow (Ba) ; (*δ.*) Reddish grey (Co, Ni, Bi) ; (*ε.*) Bluish (Pb, Zn, Cd) ; (*ζ.*) Grey (Fe, Mo, W, U, Mn, Sb), and (*η.*) White, which includes nearly all the remainder (lunar metals).

(2.) *Taste and Smell.* The *taste* of the metals is usually astringent (metallic taste). This is probably dependent on some chemical or electrical effect set up by the action of the saliva, and is often lost when they exist in combination (as NaCl). They possess generally but little odor. Iron, copper, and some other metals when rubbed give out a peculiar smell, and arsenicum when heated emits a garlic odor.

(3.) *Lustre.* In their massive and polished condition, but not when finely divided, the metals generally possess a "metallic lustre," depending on the almost total reflexion of the rays of light from their surface. Certain metalloids, moreover, also possess a certain degree of lustre, as *e.g.*, iodine, silicium, graphite, etc.

(4.) *Opacity.* The metals are almost perfectly opaque to light. Fine gold leaf, however, is said to transmit a green light (Faraday, Med. Gazette, Vol. 1, 1845) ; silver leaf, a purple light ; mercury, a blue light ("Chemical Gazette," February 1, 1846). We must be careful not to confound the passage of light through cracks, accompanied by the phenomena of diffraction, with the actual transparency of the metal.

(5.) *Texture.* (*α.*) Some metals have a fibrous texture (Fe) ; (*β.*) some are lamellated (Zn, Bi, Sb) ; (*γ.*) some are crystalline (Cu, etc.)

(6.) *Crystalline form.* Most metals may be made to crystallise. The crystals may be formed by such means as the following :—

(*α.*) By fusion and slow cooling (Bi, Pb).

(*β.*) By precipitation with another metal or non-metal (Ag by Hg or P ; Pb by Zn, etc.).

(*γ.*) By sublimation (As).

(*δ.*) By solution (tin as in the moirée metallique ; gold from an ethereal solution).

(*ε.*) By electrolysis.

The crystals generally belong to the cubic system, but they are sometimes found in rhombohedra and hexagons, as *e.g.*, zinc, arsenicum, antimony, nickel. ("Chemical Gazette," 1848, p. 165.)

(7.) *Hardness.* This, at common temperatures, varies greatly. (*α.*) Hydrogen is believed to be a gaseous metal, whilst (*β.*) mercury is liquid, and gallium melts by the heat of the hand. (*γ.*) Some are so soft that they can be indented with the nail (K, Na). (*δ.*) Others can be cut with a knife (Pb, Au, Ag); (*ε.*) whilst the majority are extremely hard (Sn, W, Fe, Ir, etc.).

The same metal may present great differences in its hardness. Thus iron may be rendered sufficiently soft to be cut with a steel saw, or so hard as to scratch glass.

(8.) *Elasticity and Sonorousness.* The sound-giving power of a body is intimately associated with its elasticity, or "property of returning to its original shape when disturbed."

(α.) Some metals are very elastic (Fe, Mn, Al, Ag); (β), others bend, but when let go do not return to their original shape (Pb, Sn, etc.), whilst (γ) others are brittle (As, Bi, etc.)

(9.) *Malleability, i. e.*, "The property of forming thin leaves when hammered or rolled." (α.) Some metals are very malleable. The following is the order of the malleability of the malleable metals, commencing with those in which the property is most marked, viz., Au, Ag, Cu, Pt, Pd, Fe, Al, Sn, Zn, Pb, Cd, Ni, Co. The alkaline metals and frozen mercury are also malleable. (β.) The remaining metals are not malleable.

(10.) *Ductility, i. e.*, "The property of being drawn into fine wire." Ductility is closely but not necessarily related to malleability. Iron is a less malleable metal than copper, but more ductile. Tin is less ductile than zinc, but more malleable.

The order of the ductility of the ductile metals, beginning with those most ductile, is as follows—Au, Ag, Pt, Fe, Cu, Pd, Cd, Co, Ni, Al, Zn, Sn, Tl, Mg, Li.

Some *non-metallic bodies,* in a state of fusion, are also very ductile, such as sulphur.

(11.) *Tenacity, i. e.,* "The property of resisting weight." This is measured by the weight a given sized wire can support, the weights being added as nearly as possible within the same time. Lead being taken as 1, the following numbers represent the relative tenacity of certain metals—Pb 1 ; Cd 1·2 ; Sn 1·3 ; Au 5·6 ; Zn 8·0 ; Ag 8·5 ; Pt 13 ; Pd 15 ; Cu 17 ; Fe 26. This tenacity is influenced by many circumstances, as, *e.g.*—(α.) By the *purity* of the metal. (β.) By the *temperature.* Thus heat diminishes tenacity. Iron is more tenacious when heated to 212° F. (100° C.) than when cold, but when heated above this temperature, its tenacity becomes less. (γ.) By *annealing.* Thus the tenacity of gold, by annealing, may be reduced by one-half; platinum, by one-third ; iron, by one-fourth, etc.

(12.) *Brittleness, i. e.,* "The property of breaking into small pieces when hammered." This varies greatly. The disintegration of gold or copper requires great force, whilst bismuth and antimony are, on the contrary, very brittle. Brittleness is frequently influenced by temperature. Thus, cold zinc is brittle, whilst hot zinc is malleable.

(13.) *Specific Gravity.* This varies greatly. Thus lithium has one-half the specific gravity of water, and platinum twenty-one times its density. (*See* Table of Elements.) It will be noticed that the *lightest* metals, such as K, Na and Li, are the *most* oxidizable, whilst the *heaviest,* such as Pt, Ir, etc., are the *least* oxidizable. It has been remarked that the specific gravity is increased by hammering and rolling.

(14.) *Thermotic Properties.* (*a.*) *All metals expand by heat and contract by cold.* Lead, however, after it has been heated, does not, on cooling, return to its original size. Each metal possesses its own rate of expansion. The expansion of any given metal is fairly uniform for equal increments of heat up to 212° F. (100° C.), but beyond this point the expansion becomes irregular.

(*β.*) *All metals conduct heat*, but their conductivity varies. Thus, if the conduction power of silver be taken as 100, copper equals 74, iron 12, lead 9, platinum 8, bismuth 2, etc. In estimating the conductivity of a metal for heat, its specific heat must always be taken into account.

(*γ.*) *Fusibility*, *i. e.*, "the property of changing from a solid to a liquid state by the action of heat," (*fundo*, I pour out).—The melting points of the metals vary greatly. Thus, mercury fuses at —37° F. (—38·8° C.) ; gallium at 86° F. (30·1° C.) ; sodium and potassium between 143° and 212° F. (60° and 100° C.) ; silver, copper, and gold at a bright-red heat (1832° to 2012° F., or 1000° to 1100° C.); iron at a white heat (2732° to 4462° F., or 1500° to 2500° C.) ; whilst others, such as platinum, etc., need the heat of the oxy-hydrogen blow-pipe or voltaic arc to effect fusion. Osmium has never been melted.

Welding implies the property possessed by certain metals of uniting by pressure, when brought to the pasty state, that is, a stage previous to complete fusion (*e. g.*, Fe, Pt, Tl, Li, K, Pd).

(*δ.*) *Volatility*, *i. e.*, "the property of being converted by heat into vapor," (*volo*, I fly).

1. Some metals are volatile at ordinary temperatures (Hg).
2. Others are volatile below redness (K, Na, As). In the case of arsenicum, it volatilizes before it melts ; hence, in order to effect fusion, the heat must be applied to the metal under pressure.
3. Others are volatile in an ordinary fire (Mg, Zn, Cd).
4. Others are volatile by the heat of the blast furnace (Cu, Pb, Ag).
5. Others are *almost*, but not absolutely non-volatile (Au, Pt).

(*ε.*) *Specific heat* (*see* page 45).

If *equal weights* of the metals be taken, the specific heat will be found to *vary* with the metal ; but if *atomic weights* of the metals be taken, the specific heat (or *atomic heat*, as it is called in this case) will be found in all cases to be equal, or nearly so.

(15.) *Electrical Properties.* (*a.*) *Conductivity.* All metals conduct electricity, but their electric conductivities are unequal. Thus, the power of silver and copper is five times as great as that of iron or of platinum, and twelve times that of lead. Hydrogen is not an electrical conductor, but it is to be noted that the vapors of the metals generally are not conductors.

(*β.*) *The metals, when liberated from their compounds, appear at the negative pole of the battery* (Electro-positives). (Page 2.)

(16.) *Magnetic Properties.* (α.) Certain metals are magnetic at ordinary temperatures, their magnetic power being generally increased by cold (Fe, Ni, Co). (β.) Other metals are attracted equally by either pole of a magnet. If such metals, in the form of a bar, be suspended over the poles of a horseshoe magnet, they arrange themselves *axially* ; that is, with their ends over each pole (Fe, Ni, Co, Mn, Cr, Pd, Pt, Os). Such metals are called *magnetics.* (γ.) Other metals are *repelled* by a magnet. When bars of such metals are suspended over the poles of a horseshoe magnet they arrange themselves *equatorially* ; that is, contrary to the poles (Bi, Sb, As, Zn, Pb, Sn, Hg, Au). Such metals are called *diamagnetics.*

(17.) *Power of absorbing gases* (occlusion). Thus, platinum and iron at a red heat absorb hydrogen freely (Deville and Troost). Platinum is capable of absorbing 3·8 volumes of hydrogen at a red heat, whilst palladium absorbs at a heat below 212° F. (100° C.) 643 times its volume.

This power of hydrogen (hydrogenium) to form an alloy, and its near relationship in this state to the metals (as, *e.* ., its power of conducting heat and electricity, its magnetic properties, etc.) have led chemists to regard hydrogen gas as the vapor of a highly volatile metal.

II. Chemical Properties.—The metals being elements, resist decomposition. We shall consider first of all their combination with oxygen.

(1.) *Action of Oxygen.*—All the metals may be oxidised, and often in several proportions. The oxides are closely analogous to the chlorides ; oxides being regarded as substitution derivatives of one or more molecules of H_2O, and chlorides as derivatives of one or more molecules of HCl. There are, however, certain oxides, as PbO_2, without chlorine analogues. The oxides generally are opaque, earthy-looking bodies, destitute of metallic lustre.

A *hydroxide* is a compound where only a part of the hydrogen of one or more molecules of water is replaced by a metal. Thus, K′ being a monad and Ca″ a dyad—

$$KHO = \text{potassic hydroxide} \; ; \; Ca'' (HO)_2 \text{ or } CaH_2O_2 = \text{Calcic hydroxide.}$$

The soluble hydroxides have a strong alkaline reaction.

All metals except gold, platinum, iridium, rhodium, and ruthenium are capable of direct combination with oxygen—that is, of combination without the intervention of a third element. The circumstances influencing the rapidity of their oxidation are (α) *the presence of moisture*, pure dry oxygen having but little action on the metals, except upon the alkaline metals, at ordinary temperatures ; (β) *the temperature ;* and (γ) *the physical condition of the metals ;* that is, whether they be finely divided or massive.

It is to be noted that *the lightest metals* (as Na, K, etc.) are those *most easily oxidized,* whilst the *heaviest metals* (as Au, Pt, etc.) are those *least easily oxidized.* Thus the attraction of a metal for oxygen is for the most part inversely as its specific gravity. In the case of mercury both oxidation and deoxidation may be easily effected by heat. We may classify the action of oxygen on the metals as follows :—

(A.) *Metals that combine with oxygen readily but part from it with difficulty.* Of these there are several classes:—

1. Metals that combine with the oxygen of the air or of water *at ordinary temperatures,* liberating hydrogen in the case of the water (K, Na, Li, Ba, Sr, Ca).
2. Metals that combine with atmospheric oxygen slowly, and with the oxygen of water only when heated (Mg, Zn, Al, Cd, Mn, Ni, Co, Fe). These metals decompose HCl and H_2SO_4 at common temperatures, liberating hydrogen.
3. Metals that combine with atmospheric oxygen very slowly, and with the oxygen of water only when the metal is at a red heat (Sb, As, Sn). These metals will not decompose HCl and H_2SO_4 at common temperatures, but will decompose KHO liberating hydrogen.
4. Metals that combine with atmospheric oxygen slowly at ordinary temperatures and rapidly when red-hot, but will not decompose water at any temperature (Cu, Pb, Bi). These oxides cannot be decomposed by heat alone.

(B.) *Metals that combine with oxygen with difficulty and part from it readily* (noble metals).

(2.) *Action of the Haloid Elements.—Chlorine* combines *directly* with all the metals, and often at common temperatures (as *e.g.*, with Sb), (*see* page 94). Bromine, iodine, and fluorine also combine with most metals directly.

(3.) *Action of Carbon.*—Iron, manganese, palladium, iridium, and a few other metals, form compounds with carbon, called *carbides* (*q.v.*). The carbides are generally more fusible than the metals themselves.

(4.) *Action of Phosphorus.*—Phosphorus combines with the metals to form *phosphides* (*q.v.*).

(5.) *Action of Nitrogen.*—The affinity of nitrogen for the metals is slight, the compounds formed, called *nitrides* (*q.v.*), being usually explosive and difficult of examination. They are generally prepared by the action of ammonia on various oxides (Au, Ag, Pt, Cu, Hg, Fe), but in the case of vanadium, titanium, and molybdenum, direct union of the metal and nitrogen may be effected.

(6.) *Action of Hydrogen.*—Hydrogen forms *hydrides* (*q.v.*) with several of the metals (As, Sb, Cu, Fe, K, Na, Pd).

(7.) *Silicon, boron, selenium,* and *tellurium* also combine with certain of the metals to form *silicides, borides, selenides,* and *tellurides* (*q.v.*).

(8.) *Action of Water on the metals* :—

(*α*.) Certain metals decompose water at *common temperatures* (K, Na, Li, Ba, Sr, Ca).

(*β*.) Others only when *the water is boiling* (Mg, Al, Cd, Mn).

(*γ*.) Others, when the metal is *red* hot (Sb, As, Sn, Zn, Fe, Cr, Co, Ni).

(*δ*.) Others when the metal is *white* hot (Al, Pb, Bi, Cu).

(*ε*.) Others do not decompose water (noble metals).

The action of the metals on water is modified (1) by *the presence of air*, whereby the action of a metal on water is rendered more energetic ; and (2) by *the contact of two metals*, whereby a galvanic current may be set up, and the energy of solution intensified.

(9.) *Action of the Acids on metals* :—

(A.) *Sulphuric Acid.*—(*α*.) Sulphuric anhydride cannot be made to combine directly with the metals.

(*β*.) The *concentrated* acid acts on very few metals *without heat*, whilst,

(*γ*.) The *dilute* acid acts on most metals at ordinary temperatures, a metallic sulphate being formed with the liberation of hydrogen (Zn, Fe, Co, Ni, Mn).

(*δ*.) In certain cases heat is required to bring about combination with the dilute acid, when a metallic sulphate is commonly formed and sulphurous acid liberated (Ag, Cu, Hg, As, Sb, Bi, Sn, Pb) ($Ag_2 + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2$).

(*ε*.) The acid (strong or dilute) has no action on gold, platinum, rhodium, or iridium. Thus, sulphuric acid is used to part silver or copper from gold.

(*ζ*.) When the vapor of sulphuric acid is passed over red hot platinum, it is decomposed into oxygen and sulphurous acid (*see* p. 72).

(B.) *Nitric Acid.*—Nitric acid dissolves most metals, and more readily when dilute than concentrated. (*a*.) Upon *gold and platinum* nitric acid has no action ; whilst (*b*) *tin and antimony* are not dissolved but oxidised by nitric acid, the insoluble anhydrides SnO_2 and Sb_2O_5 being formed.

We may here note that whilst dilute sulphuric acid by its action on the metals usually liberates hydrogen, nitric acid does not liberate hydrogen. No doubt, however, hydrogen, in the case of nitric acid, is in the first instance set free, but undergoes rapid oxidation.

The products resulting from the action of nitric acid on the metals vary. We may note the following :—

(*a*.) *Nitrous Oxide* (N_2O). By the action of the dilute acid on an energetic metal, such as zinc :—

$$\underset{\text{Zinc}}{4Zn} + \underset{\text{Nitric acid}}{10HNO_3} = \underset{\text{Zincic nitrate}}{4(Zn2NO_3)} + \underset{\text{Water}}{5H_2O} + \underset{\text{Nitrous oxide.}}{N_2O.}$$

(β.) *Nitric Oxide* (NO). By the action of an acid of specific gravity 1·25 on such metals as Cu and Hg :—

$$3Cu + 8HNO_3 = 3(Cu2NO_3) + 4H_2O + 2NO.$$

Copper + Nitric acid = Cupric nitrate + Water + Nitric oxide.

(γ.) *Nitrous Anhydride* (N_2O_3). By the action of the acid on silver or palladium :—

$$2Ag_2 + 6HNO_3 = 4AgNO_3 + 3H_2O + N_2O_3.$$

Silver + Nitric acid = Argentic nitrate + Water + Nitrous anhydride.

(δ.) *Nitric Peroxide* (N_2O_4). By the action of an acid of specific gravity 1·42 on tin, copper, etc.:—

$$5Sn + 20HNO_3 = Sn_5O_{10},5H_2O + 5H_2O + 10N_2O_4.$$

Tin + Nitric acid = Metastannic acid + Water + Nitric peroxide.

(ε.) *Nitrogen.* By the action of the acid on copper at a high temperature :—

$$5Cu + 12HNO_3 = 5(Cu2NO_3) + 6H_2O + N_2.$$

(ζ.) *Ammonia* (NH_3). Any metal capable of decomposing water will generate ammonia with dilute nitric acid. (*a.*) In the first stage nascent hydrogen is set free. (β.) This reacts on the nitric acid, forming water with the oxygen, and ammonia with the nitrogen ; (γ.) and lastly, the excess of ammonia combines with the excess of acid. Thus :—

(*a.*) $2HNO_3 + Zn = Zn2NO_3. + H_2.$

Nitric acid + Zinc = Zinc nitrate + Hydrogen.

(β.) $2HNO_3 + 3H_2 = NH_3 + 3H_2O.$

Nitric acid + Hydrogen = Ammonia + Water.

(γ.) $2HNO_3 + 2NH_3 = 2NH_43NO_3.$

Nitric acid + Ammonia = Ammonic nitrate.

(C.) *Hydrochloric Acid.* — The affinity of a metal for chlorine is somewhat greater than its affinity for oxygen ; hence the action of hydrochloric acid on a metal is always a little in excess of the action of water on the metal. All metals that decompose water at a red heat, decompose hydrochloric acid, hydrogen being liberated and a chloride of the metal formed ($2HCl + Zn = ZnCl_2 + H_2$). It is to be noted that—

(*a.*) *Silver* does not decompose water at any temperature, but is *slowly* dissolved by strong hydrochloric acid.

(β.) *Gold and Platinum* are not acted on by hydrochloric acid, unless free chlorine be present.

(D.) *Nitro-muriatic Acid* (aqua regia).—This is a mixture of one part of HNO_3 and three parts of HCl. Gold, platinum and the noble metals generally are dissolved by it, free chlorine, together with red fumes [*viz.*, the oxy-chlorides of nitrogen (NOCl and $NOCl_2$)] being evolved.

(E.) *Hydrosulphuric Acid* (sulphuretted hydrogen).

(α.) On certain metals sulphuretted hydrogen acts *at ordinary temperatures* (Hg, Ag); whilst

(β.) On other metals the action does not occur without heat, when the displacement of the hydrogen from the H_2S may be either

(1.) *Complete, e.g.,* $H_2S + Sn = SnS + H_2$, or
(2.) *Partial, e.g.,* $2H_2S + 2K = 2KHS + H_2$.

(10.) *Action of Alkalies.* Certain metals, such as iron and copper, when red hot decompose ammonia gas. When potassium is gently heated in dry ammonia, KH_2N is formed, which may be regarded either as a substitution derivative of H_3N, or a compound of potassium and amidogen (H_2N).

Platinum as well as other metals are oxidised when heated with potassic hydrate.

Classification of the Metals.—The classification of the metals according to their *atomicity* has manifest advantages. The table (page 51) illustrates their arrangement accordingly.

We prefer, however, (regarding the primary object of classification as convenience,) to adopt simply a division into the various groups such as occur in the ordinary process of systematic analysis, commencing with the alkaline metals.

CHAPTER XII.

ALLOYS AND SALTS.

Alloys—Changes in property effected by Alloying—Acids—Bases—Salts—Varieties of Salts. Haloid Salts.—Oxides, Chlorides, Bromides, Iodides, Fluorides, Sulphides, Nitrides, Arsenides, Selenides, Tellurides, Phosphides, Carbides, Borides, Silicides, Hydrides. *Oxy-Salts*—Sulphates, Selenates, Tellurates, Chromates, Manganates, Tungstates, Molybdates, Stannates, Thiosulphates, Sulphites, Selenites, Dithionates, Nitrates, Nitrites, Hyponitrites, Chlorates, Bromates, Iodates, Perchlorates, Periodates, Chlorites, Hypochlorites, Phosphates, Hypophosphites, Phosphites, Arsenates, Vanadates, Antimonates, Sulphantimonates, Arsenites, Antimonites, Sulpharsenites, Sulphantimonites, Carbonates, Silicates, Borates. *Double Salts.*

WE proceed to consider :—

I. The compounds formed by the union of metals with metals (alloys and amalgams).

II. The compounds of the non-metals with the metals (salts).

ALLOYS (*ad* to, and *ligo* I bind).

Definition.—An alloy is a compound formed by the union of two or more metals. If the alloy contains mercury, it is then called an *amalgam.*

Are the alloys mere mechanical mixtures, or are they chemical compounds? To answer this question we must ask, Is there any evidence of *definite change* resulting from admixture of metals, similar to what happens in the case of combinations with the non-metals? Matthiessen (who specially studied the subject) considered that alloys might be divided into two classes :—

(1.) *Physical Alloys, i.e.*, a mere mechanical mixture of metals, in which, at the time of mixture, no heat is evolved, and where each metal imparts to the alloy its properties in the proportion in which it exists in the alloy. As illustrations of this class we may mention alloys of lead and tin, of zinc and cadmium, etc.

(2.) *Chemical Alloys, i.e.*, where, at the time of mixture, heat is evolved (sodium and mercury), the metals forming the alloy not imparting their properties to the alloy in that proportion in which they are present. This class includes alloys of all the metals, excepting mixtures of lead, tin, zinc, and cadmium amongst themselves.

Definite compounds of metals with metals no doubt exist. Necessarily, however, intensity of combination being largely dependent on dissimilarity in the property of the constituents, the ties of union in the case of the metals, standing as they do near each other in the electro-chemical scale, are weak, and the separation of the components easy.

Thus (1) heat will drive off zinc from its alloy with copper, and arsenicum from its alloy with platinum; whilst (2) slight mechanical causes, such as the mere squeezing through leather, will remove an excess of mercury from a mixture of mercury and silver.

Change of property is the distinguishing feature of the chemical act. We shall consider the changes that manifest themselves as the result of a combination of metals.

I.—Changes in the Sensible and Physical Properties of Alloys.

(*α*.) *Color.* Thus the addition of 18 per cent. of nickel to brass renders it white (Packfong, or German silver). Similarly, the admixture of arsenicum with copper, or of platinum or of palladium with gold, renders the copper and the gold white. The alloy of gold and silver has a pale greenish tint.

(*β*.) *Hardness.* The hardness of an alloy is usually greater than the mean hardness of the constituent metals. Thus a little copper (8·33 per cent.) is added to the gold used for coinage, in order to increase the hardness of the gold. The alloy of tin, lead, and antimony forms a hard *type-metal.* The alloy of copper and zinc forms a hard compound that may be cast or turned. The alloy of copper and tin forms a very hard bronze. Manganese or tungsten increases the hardness of steel to such an extent that the alloy is used in the construction of instruments for boring steel.

(*γ*.) *Elasticity and Sonorousness.* An alloy of copper and tin ($=Cu_6Sn$), or of copper, zinc and lead, constitutes the sonorous *bell-metal.*

(*δ*.) *Malleability.* The malleability of a metal is usually decreased by alloying. Thus, if 0·5 gr. of lead be added to 1 oz. of gold, its malleability is destroyed. If melted gold be kept for some time in the vicinity of melted tin, the gold becomes brittle. An alloy of two malleable metals may form a brittle alloy (*e.g.*, gold and lead), but no case is known where the alloy of two brittle metals forms other than a brittle alloy. A mixture of copper, zinc, and platinum forms a very malleable alloy; but if a trace of iron be added, in the proportion of 0·5 gr. of iron to 4 oz. of the alloy, it renders the alloy brittle.

(*ε*.) *Tenacity.* This may be either increased or diminished:—

(1.) *Increased.* If a gold wire be taken capable of bearing a strain of 25 lbs., it will be found that a similar sized one of copper will bear a weight of 25 to 30 lbs. If now a wire of the same gauge be made of an alloy of gold with 8·4 per cent. of copper, it will be found to bear a strain of from 70 to 75 lbs.

(2.) *Diminished.* If a copper wire be taken which bears a strain of from 25 to 30 lbs., the same sized tin wire will be found to bear a strain of less than 7 lbs., whilst a wire formed by an alloy of equal parts of tin and copper will also not bear a greater strain than 7 lbs.

(ζ.) *Specific Gravity.* The specific gravity of an alloy may be either *above* or *below* the mean of its constituents. Standard gold consists of 11 parts of gold and 1 of copper, the specific gravity of which alloy is 17·157, although the mean specific gravity is 18·47.

(η.) *Thermotic properties.* The fusing-point of an alloy is invariably below the mean fusing points of its constituents, just as the fusibility of double chlorides, carbonates, or silicates, is generally lower than the separate salts of which these double salts are composed. Thus an alloy of four parts of bismuth (which fuses at 507° F., or 264° C.), two of lead (which fuses at 607° F., or 309·5° C.), and one of tin (which fuses at 442° F., or 227·8° C.) (such mixture nearly corresponding to the formula Bi_2PbSn), is found to melt below 212° F. (100° C.). Platinum, which is very difficult of fusion, melts easily when alloyed with arsenicum. In the extraction of silver from lead by Pattinson's process (*see* Index), it is found that the part which cools last contains nearly all the silver, owing to the greater fusibility of the alloy of lead and silver.

(θ.) *The conductivity of metals for heat and electricity* is usually decreased by alloying.

II. Changes in the Chemical Properties.

The alterations of chemical properties in the case of alloys are not well marked :—

(1.) *A certain change in the capacity of a metal for oxidation may be noted.* An alloy, *e.g.*, of two oxidizable metals (such as of lead and tin) is generally more easily oxidized than either of the constituents.

(2.) *A change in the action of acids on the alloy may be remarked.* For example—German silver is soluble in dilute sulphuric acid, although the acid does not attack copper, which is one of its chief constituents. An alloy of 1 part of platinum and 12 parts of silver is soluble in nitric acid, in which the platinum is insoluble. Further, the presence of iridium and rhodium in platinum, as commonly occurs in the metal found in commerce, renders the platinum less easily attacked by chemical reagents.

SALTS.

Acids, Bases, Salts.

Chemical nomenclature, prior to 1786, was both unsystematic and imperfect. *Acetic acid* to the older chemists was a mineral acid, because it was sour. A *salt* was regarded as a solid, crystallizable substance, soluble in water.

In 1786 Lavoisier defined an acid as "*an oxidized body, sour, capable of reddening vegetable blues, and of combining with and neutralizing alkalies.*" All the acids known to Lavoisier contained oxygen ; he regarded this element, therefore, as the acidifying principle of an acid, and essential to its existence (acid-begetter). A salt Lavoisier defined as "*the union of an acid*"—that is of "an anhydride," as we call it, but which Lavoisier and his school regarded as an acid—"*with an oxide of a metal*" (a base). Thus KO,SO_3, formed the salt sulphate of potash. This constituted "*the dualistic theory of salts.*"

In 1795 Sir H. Davy pointed out that the very type of all salts (viz. common salt) contained neither acid nor base, and that there were numerous compounds corresponding in all points to Lavoisier's definition of an acid, except that they contained no oxygen. Hence Lavoisier's definition of acids and salts had to be modified. Acids were consequently divided into two classes, and salts into two classes, viz.:—

(1.) *Oxy-acids;* bodies containing oxygen, which, combined with an oxide of a metal (a base), formed *oxy-salts.*

(2.) *Hydr-acids;* bodies in which hydrogen was an essential ingredient, the combination of the radical or characteristic element of which with metals, formed *haloid salts.*

In 1812, that is, very shortly after the discovery of chlorine, Davy recognized the similarity in the action of oxy-acids and of hydr-acids on metals. He further pointed out that all acids contained hydrogen, and that an anhydride was not an acid. He suggested that all acids were salts, and that all salts were compounds of a radical (simple or compound) with a metal. He thus laid the foundation of "*The Binary Theory of Salts.*" Lavoisier's "*Dualistic Theory*" expressed *nitrate of potash* as KO,NO_5, or a compound of the *acid* (as he regarded it) NO_5 and the *base* KO; whilst Davy's "*Binary Theory*" expressed it as KNO_6, or a compound of the *metal* potassium (K) with the *acid radical* NO_6. Moreover Davy remarked on the close similarity of constitution between oxy-salts and haloid salts, as, for example, between KCl and KNO_6.

In 1819, Berzelius introduced his Electro-Chemical Theory, according to which he regarded salts as compounds of an *electro-negative* (that is, a body attracted by the *positive* pole of a battery), with an *electro-positive* (that is, a body attracted by the *negative* pole). All the non-metals (excepting hydrogen) were electro-negative; all the metals (including hydrogen) were electro-positive. This much remains a fact, viz., that the elements differing most in their chemical relationship usually exhibit the greatest activity of combination; but, that the chemical functions were determined *exclusively* by the electrical relationships, was disproved by the discoveries of 1834 and following years. For *the laws of substitution* (introduced and elaborated by Dumas, Gay Lussac, Laurent, Gerhardt, etc.) prove the possibility of an electro-negative body like chlorine taking the place of an electro-positive body like hydrogen in a compound. The "theory of types" was then called in, to aid the "theory of substitution."

We shall here discuss the definitions of (I.) *an acid,* (II.) *a base* (III.) *a salt.*

I. Acids (ακη, a point).

An Acid is *"a compound containing one or more atoms of hydrogen, capable of displacement by a metal presented to it in the form of a hydrate."* Acids are of different basicities, according to the number of atoms of displaceable hydrogen they contain :—

A *monobasic acid* contains one atom of *displaceable hydrogen,* that is, of hydrogen that may be displaced by a metal, *e.g.* :—

HNO_3 (nitric acid) forms KNO_3, $NaNO_3$, $Ca''2(NO_3)$.
HCl (hydrochloric acid) forms KCl, $NaCl$, $Ca''Cl_2$.

A *polybasic acid* contains two or more atoms of displaceable hydrogen. It is called *dibasic* when it contains two atoms of displaceable hydrogen (*e.g.*, H_2SO_4); *tribasic* when it contains three atoms (*e.g.*, H_3PO_4); and so on.

Types of Different Acids.

(1.) (*a.*) *A monobasic acid* has been regarded as formed on the type of *a single molecule of water* $\left(\left.\begin{matrix}H\\H\end{matrix}\right\} O\right)$ where *one* hydrogen atom of the water molecule has been displaced by a compound monatomic radical.

(*β.*) *The anhydride of such monobasic acid* is regarded as formed by the displacement of *both* hydrogens of the water molecule by two molecules of the compound radical.

(*γ.*) *The salt of such monobasic acid* is regarded as formed by the displacement of the *second* hydrogen atom of the acid, by a metal.

Illustrations of *a*, *β*, and *γ*, will be seen as follows :—

$$(a.)\quad \left.\begin{matrix}NO_2\\H\end{matrix}\right\} O = HNO_3 \ (\textit{acid}).$$

$$(\beta.)\quad \left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\} O = N_2O_5 \ (\textit{anhydride}).$$

$$(\gamma.)\quad \left.\begin{matrix}NO_2\\K\end{matrix}\right\} O = KNO_3 \ (\textit{salt}).$$

(2.) (*a.*) *A dibasic acid* has been regarded as formed on the type of *a double molecule of water* $\left(\left.\begin{matrix}H_2\\H_2\end{matrix}\right\} O_2\right)$, where two hydrogen atoms of the double water molecule have been displaced by a compound diatomic radical.

(*β.*) *The anhydride of such dibasic acid* is formed by the displacement of the four hydrogen atoms by two atoms of the compound diatomic radical.

(*γ.*) *The salt of such dibasic acid* is formed by the displacement of one or both hydrogen atoms of the acid by a metal.

If one of the hydrogens only be displaced by a metal, *an acid salt* is formed ;—if both hydrogens be displaced by the same metal then a *normal salt* is formed ; whilst if the hydrogens be displaced by different metals, then one variety of a *double salt* is formed. Thus—

$$(\alpha.)\quad \left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2 = H_2SO_4\ (\textit{acid}).$$

$$(\beta.)\quad \left.\begin{matrix}SO_2\\SO_2\end{matrix}\right\}O_2 = 2SO_3\ (\textit{anhydride}).$$

$$(\gamma.)\quad \left.\begin{matrix}SO_2\\KH\end{matrix}\right\}O_2 = KHSO_4\ (\textit{acid salt}).$$

$$\left.\begin{matrix}SO_2\\K_2\end{matrix}\right\}O_2 = K_2SO_4\ (\textit{normal salt}).$$

(3.) Similarly, a *tribasic acid* is regarded as formed on a treble water type $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$; (*a*) *the acid* resulting when the H_3 is replaced by a triatomic compound radical ; (*β*) *the anhydride* when the $2H_3$ is replaced by two atoms of the triatomic radical ; and (*γ*) *the salts* when one or more of the hydrogens of the acid is replaced by a metal. Thus—

$$(\alpha.)\quad \left.\begin{matrix}PO\\H_3\end{matrix}\right\}O_3 = H_3PO_4\ (\textit{acid}).$$

$$(\beta.)\quad \left.\begin{matrix}PO\\PO\end{matrix}\right\}O_3 = P_2O_5\ (\textit{anhydride}).$$

$$(\gamma.)\quad \left.\begin{matrix}PO\\Na_3\end{matrix}\right\}O_3 = Na_3PO_4\ (\textit{salt}).$$

II. Bases.

A Base is "*a compound body capable of being converted into a salt by the action of an acid, and of thereby more or less neutralizing the reactions of the acid.*" Bases may be divided into three classes :—

(1.) *Compounds of metals with oxygen*, such as baryta (BaO), lime (CaO). A metal usually forms but one oxide capable of producing salts with acids ; but to this general rule there are many exceptions. Thus—

The *protoxide of iron* (FeO) forms salts (*e.g.*, FeO,SO_3) distinguished as *protosalts*, or more commonly as *ferrous salts*.

The *peroxide of iron* (Fe_2O_3) forms salts (*e.g.*, $Fe_2O_3,3SO_3$) distinguished as *persalts*, or more commonly as *ferric salts*.

(2.) *Compounds of metals with the compound radical hydroxyl* (HO) (*hydroxides, e.g.*, sodic hydrate NaHO (soda) ; potassic hydrate KHO (potash), etc.). A hydroxide consists of one or more water molecules, where one or more of the hydrogens are replaced by a metal. Thus—

$$\left.\begin{matrix}K'\\H\end{matrix}\right\}O = K'HO\ ;\qquad \left.\begin{matrix}Ca''\\H^2\end{matrix}\right\}O_2 = Ca''H_2O_2.$$

The soluble hydroxides are called *alkalies*, and have the power of blueing red litmus.

(3.) *Certain compounds with nitrogen, phosphorus, arsenic, and antimony*, such, for example, as ammonia (NH_3).

III. Salts.

A Salt is "*a compound formed by the mutual action of an acid and a base*." The name given to the salt depends on the base and acid present. Thus sodium nitr*ate* implies a salt formed by a combination of sodium and nitr*ic* acid ; sodium nitr*ite*, a salt formed by a combination of sodium and nitr*ous* acid.

Salts are binary compounds, containing (to use convenient language) an electro positive and an electro negative constituent. Thus NaCl is the type of *haloid salts*, where the metal sodium is in direct contact with the halogen chlorine.

VARIETIES OF OXY-, SULPHO-, AND DOUBLE SALTS.

(1.) **Oxy-Salts.** *Compounds formed from an oxygen acid, by the displacement of all or a part of its hydrogen by a metal or by a compound radical.* Of these we recognize several classes as follows :—

(*a.*) *Normal Salts*, i.e., *a salt where all the displaceable hydrogen of the acid is exchanged for an equivalent amount of a metal or of a positive compound radical.* Thus, for example,

K_2SO_4 from H_2SO_4 ; $NaNO_3$ from HNO_3 ; $Ca''_3 2(PO_4)$ from $2H_3PO_4$.

A *normal* salt was formerly termed a *neutral* salt, that is, a salt which neither reddens blue-litmus nor blues red-litmus. Neutrality, however, depends more on chemical energy than on actual proportion. Thus $ZnSO_4$ reddens *blue* litmus, and Na_2CO_3 blues *red* litmus, whilst other normal salts, such as KNO_3, are strictly neutral. Yet in none of these is any free acid or base present.

(*β.*) *Acid Salts*, i.e., *a salt in which the displaceable hydrogen of the acid is only partially exchanged for a metal or positive compound radical.* Acid salts are invariably salts of polybasic acids. All acids, the hydrogen of which plays the part of a metal atom, are, in a sense, salts. Thus—

$KHSO_4$ is derived from H_2SO_4 ; HNa_2PO_4 from H_3PO_4.

(*γ.*) *Basic Salts*, i.e., *a salt where the quantity of the metal or compound radical exceeds the number of the atoms of displaceable hydrogen in the acid.* In other words, where the proportion of base present predominates over or is in excess of the acid. Thus—

$HgSO_4,2HgO$ = Turpeth Mineral.
$CuCO_3,CuH_2O_2$ = Malachite.
$2PbCO_3,PbH_2O_2$ = White lead.

(2.) **Sulpho-Salts.**—*Compounds analogous to oxysalts, but containing sulphur in the place of oxygen.* Thus—

Sodic sulph-arsenate; $3Na_2S,As_2S_5$, or Na_3AsS_4;
Argentic sulph-arsenite; Ag_3AsS_3.

(3.) **Double Salts.**—*Compounds where the displaceable hydrogens of the acid are exchanged by different metals or compound radicals.* Thus Rochelle salt is a compound formed from tartaric acid ($H_2C_4H_4O_6$) in which the two atoms of displaceable hydrogen are displaced by an atom of sodium and of potassium respectively ($KNaC_4H_4O_6$).

Double salts may be formed, and more often are formed, from oxides of different classes. Thus common alum consists of potassium and aluminium sulphate, $K_2SO_4,Al_23SO_4 = K_2Al_24SO_4$. Double salts may also be formed by a combination of haloid salts. Thus $2KCl,PtCl_4$ forms potassium platinic chloride. These combinations are regarded as molecular rather than atomic.

The terms *oxychloride, oxyiodide,* etc., imply compounds formed by the union of one or more molecules of a metallic oxide with a molecule of a chloride, iodide, etc., of the same metal. Thus the compound $PbCl_2,7PbO$ is termed oxychloride of lead (Turner's yellow).

We shall now consider, in order, the compounds of the metals with the non-metallic elements.

I.—Oxides.

Definition.—Compounds of a metal with oxygen.

Preparation of Oxides.—I. *Hydrated oxides.* By precipitating a metallic salt with an alkaline hydrate:—

$ZnSO_4$	+	$2KHO$	=	K_2SO_4	+	ZnH_2O_2.
Zinc sulphate	+	Potassic hydrate	=	Potassium sulphate	+	Hydrated zinc oxide.

II. *Anhydrous oxides.* (1.) By burning a metal in air or oxygen, as in the case of Zn, As, Pb, K, Na. (A *protoxide* may often be converted into a *peroxide* by heating it in a current of air or oxygen.)

(2.) By the ignition of—

(α.) *Nitrates;* nitric anhydride being expelled (Hg, Bi, Cu, Ba, Sr).

(β.) *Carbonates;* CO_2 being expelled. (This occurs with most carbonates, those of Cs, Rb, Na, K, Ba, Li excepted.)

(γ.) *Hydrated oxides* (Fe).

(δ.) *Sulphates* (as those of alumina, ferric oxide, etc.).

(3.) All acid oxides may be prepared by deflagrating the metal or its sulphide with nitre.

(4.) By the electrolysis of their aqueous solutions.

Varieties of Oxides.—Oxides may be divided into three classes:

I. *Basic or alkaline oxides; i.e.,* oxides that act as bases (Ag_2O,

PbO; Fe_2O_3). These bodies form hydrated oxides by combination with water (hydroxides), and possess the property of neutralizing acids, forming *salts*. When basic oxides are soluble in water, their solutions turn red litmus blue.

II. *Neutral, saline or indifferent oxides; i.e.*, oxides that exhibit very slight disposition to enter into combination (MnO_2).

III. *Acid oxides or metallic anhydrides; i.e.*, oxides (such as As_2O_3) which form acids by their combination with water.

Table of Oxides.

Names.	Formula.	Types.	Metals belonging to the group.	Characteristics of group.
I. Suboxides ..	$'M'_2O$	$'Cu'_2O$	Cu, Pb, Hg	*Basic.* A dyad metal becoming equivalent to a single H atom. Unstable bodies easily decomposed.
II. Monoxides ..	(*α.*) M'_2O (*β.*) $M''O$	Ag_2O $Ca''O$	The metals of the alkalies with Tl′, Ag′, and the metals of the alkaline earths: also Mg″, Zn″, Cd″, La″, Di″, Th″. Protoxides of Ce″, U″, Co″, Ni″, Fe″, Cr″ Mn″, Sn″, Cu″, Pb″, Hg″, Pd″.	*Basic.* The alkaline oxides combine with water to form *hydrates*, one molecule of each, forming *two* molecules of hydrate ($Na_2O+H_2O=2NaHO$). The alkaline earth-oxides also form hydrates, one molecule each of the oxide and water forming *one* molecule of hydrate ($CaO+H_2O=CaH_2O_2$).
I. Sesquioxides .	M'''_2O_3	$Al_2'''O_3$	Al, Ce, Fe, Mn, Cr, Sb, Bi, U.	Feebly *Basic.* Salts redden litmus.
			Co, Ni.	*Neutral.* Evolve Cl with HCl.
			As, Au.	Feebly *acid.*
. Three-four Oxides	M_3O_4 or $M''O+M'''_2O_3$	Fe_3O_4	Fe, Cr, U, Mn, Ni, Co, Also double oxides as FeO,Cr_2O_3 (chrome ironstone); MgO, Al_2O_3 (spinelle); ZnO,Al_2O_3 (Gahnite)	*Neutral.* By the action of acids they form $MO+M_2O_3$.
. Dioxides	(*α.*) $M^{iv}O_2$	PtO_2	Pt, Pd	Feebly *Basic.* Form hydrates ($PtO_2,2H_2O$).
	(*β.*) M'_2O_2	Na_2O_2	Na, Ag, Ba, Ca, Sr, Mn, Pb	*Neutral bodies*, or else form very unstable salts which evolve O with H_2SO_4. With HCl they either furnish hydroxyl or evolve chlorine.
	(*γ.*) $M^{iv}O_2$	SnO_2	Sn, Ti	*Acid*, as hydrates.
. Trioxides ..	$M^{vi}O_3$	CrO_3	Cr, Mo, W, Ru, Fe, Mn	*Acid* (metallic anhydrides).
I. Anhydrides..	M_2O_5	As_2O_5	As, V, Sb,	*Acid.*
II. Tetroxides	$M^{viii}O_4$	RuO_4	Ru, Os	Volatile— Oxygen easily evolved

Properties of the Oxides.—(*a.*) PHYSICAL, etc. The oxides are solid bodies of varied color, having generally a more or less metallic taste, but no smell. They are harder than the actual metals, but of less specific gravity.

Action of Heat on metallic oxides.—(A.) *Fusibility.* An oxide of a metal is generally less fusible than the metal. To this general rule there are three exceptions, viz., FeO; Cr_2O_3; MoO_3.

(i.) Some oxides are volatile at ordinary temperatures (As_2O_3; Sb_2O_3; OsO_4).
(ii.) Some oxides fuse at a red heat (K_2O; Na_2O; PbO; Bi_2O_3).
(iii.) Some oxides are infusible at a white heat (CuO; MoO_3; Cr_2O_3; Fe_3O_4).
(iv.) Some oxides need the heat of the oxy-hydrogen jet (BaO; SrO; Al_2O_3).
(v.) Some oxides are infusible (zirconia, yttria).

(B.) *Reduction.* At a red heat certain oxides are completely, whilst others are only partially, decomposed:—

(i.) *Reduction is complete* in the case of the oxides of Au, Ag, Pt, Pd, Hg, etc.
(ii.) *Reduction is partial* in the case of such peroxides as PbO_2, Co_2O_3, Ni_2O_3, BaO_2. These by heat become protoxides, viz., $Pb''O$, $Co''O$, $Ni''O$, $Ba''O$. Again, the anhydrides As_2O_5 and CrO_3 become when heated As_2O_3 and Cr_2O_3, whilst MnO_2 becomes Mn_3O_4.

(C.) *Heated in a current of hydrogen*, all the oxides may be completely reduced, excepting Al_2O_3, Cr_2O_3, MnO, and the oxides of the alkalies and alkaline earths ($CuO+H_2=Cu+H_2O$). The oxides of mercury, silver, platinum and gold are reduced at 212° F. (100° C.), and the rest at a red heat.

Note here *reciprocal action.* Free hydrogen reduces the oxide of iron, steam being formed, whilst steam passed over red hot iron yields oxide of iron and free hydrogen.

(D.) *Heated with carbon*, all the oxides may be reduced, except lithia, alumina, and the oxides of the earth-metals. In the case of the readily oxidizable metals (as K, Zn, Fe, etc.), CO is evolved, the CO_2 first produced undergoing decomposition ; whilst with the less readily oxidizable metals (such as Cu, Pb, etc.), the CO_2 evolved is not further reduced.

Action of Electricity on metallic oxides.—The protoxides are electrical insulators, whilst some of the peroxides are conductors.

Action of Water on the oxides.—The oxides of the alkaline metals, together with the oxides of barium, strontium, calcium, and thallium, and the hydrated acid oxides, are freely soluble in water ;—the oxides of lead, silver, and mercury are slightly soluble in water. The remaining oxides are insoluble.

Most oxides unite chemically with water to form hydroxides (*hydrated oxides*). All hydroxides neutralise acids. In some instances the metal will not part with its water molecule at any temperature, as in the case of the alkaline hydrates, whilst with other hydrates, heat easily effects separation.

(β.) CHEMICAL.—The chemical properties of the oxides differ, the variations depending to a great extent on the different degrees of oxidation of which the metal is capable. Thus of the oxides of manganese, MnO and Mn_2O_3 are basic oxides ; Mn_3O_4 is an indifferent oxide (that is neither basic nor acid); whilst MnO_3 and Mn_2O_7 are acid oxides. As a rule the higher the oxide, the less marked is its basic character.

Action of Chlorine on the oxides.—All metallic oxides are decomposed when heated in an atmosphere of chlorine, except magnesia and the oxides of the earths. The metal is reduced in the case of the oxides of the noble metals, whilst in other cases a metallic chloride is formed. Chlorine decomposes certain oxides, as Ag_2O, at ordinary temperatures.

In the case of the hydrated oxides of the alkalies and alkaline earths, chlorine forms with them bleaching compounds. With the hydrated oxides of iron, manganese, chromium, cobalt, and nickel, it forms either a mixture of a chloride with a hydrated sesquioxide ($3CoH_2O_2 + Cl_2 = CoCl_2 + Co_2H_6O_6$) ; or if the liquid be strongly alkaline, a sesquioxide only ($2CoH_2O_2 + 2KHO + Cl_2 = Co_2H_6O_6 + 2KCl$) ; or if the metal be capable of forming an acid, a salt results by the action of the acid on the excess of alkali ($Fe_2H_6O_6 + 10KHO + 3Cl_2 = 2K_2FeO_4 + 6KCl + 8H_2O$).

Action of Sulphur on the oxides.—At high temperatures sulphur decomposes most metallic oxides, with the exception of MgO, Al_2O_3, Cr_2O_3, SnO_2, TiO_2, and the oxides of the earths proper. In most cases a sulphide is formed, and SO_2 escapes ; whilst in the case of the oxides of the alkalies and alkaline earths, a mixture of a *sulphide* with a *sulphate* of the metal is formed.

Action of Nascent Hydrogen on the oxides.—Most oxides are decomposed by nascent hydrogen.

Action of Acids on the metallic oxides.—(1.) *Hydrochloric acid.*—In most cases, water and a corresponding metallic chloride are formed Thus—

Cuprous oxide forms *cuprous chloride* ($Cu_2O + 2HCl = H_2O + Cu_2Cl_2$).
Sesquioxides form *sesquichlorides* ($Fe_2O_3 + 6HCl = 3H_2O + Fe_2Cl_6$).
Binoxides form *tetrachlorides* ($SnO_2 + 4HCl = 2H_2O + SnCl_4$).

If chlorides corresponding to the oxides do not exist, other changes result. Thus in the case of the following oxides, the reactions noted occur :—

Antimonic oxide ; $Sb_2O_3+6HCl=3H_2O+2SbCl_3$.
Dimanganic trioxide ; $Mn_2O_3+6HCl=3H_2O+2MnCl_2+Cl_2$.
Manganese dioxide ; $MnO_2+4HCl=2H_2O+MnCl_2+Cl_2$.
Chromic anhydride ; $2CrO_3+12HCl=6H_2O+Cr_2Cl_6+3Cl_2$.

(2.) *Sulphuric Acid.*—Sulphuric acid combines with *basic oxides* to form salts, the acid displacing other acids with which the oxide may be united (page 8); whilst in the case of *indifferent* or *acid oxides*, the sulphuric acid combines with the base formed, and sets free oxygen. Thus, $2MnO_2+2H_2SO_4=2MnSO_4+2H_2O+O_2$.

In all cases where sulphuric acid acts on *oxides*, water is formed, whilst when it acts on the *metals*, hydrogen is liberated.

(3.) *Sulphuretted Hydrogen* (H_2S).—Most metallic oxides (except magnesia, alumina, and chromic oxide) are converted by H_2S into sulphides or sulph-hydrates of the metal and water—

$$PbO+H_2S=PbS+H_2O.$$

THE HALOID SALTS (CHLORIDES, IODIDES, BROMIDES, FLUORIDES).

II.—Chlorides.

Definition.—Compounds of metals with chlorine (the radical of HCl). [Chlorine also combines with the non-metals (*e.g.*, HCl, SCl_2, PCl_5), and also with radicals or groups of atoms (*e.g.*, C_2H_5Cl = chloride of ethyl, etc.).]

Natural History.—The chlorides are found in all three kingdoms of nature, chiefly in combination with the alkalies. Sodium and potassium chlorides occur in sea water and in rock salt. Mercurous chloride (Hg_2Cl_2) and silver chloride (AgCl) occur as natural minerals.

Preparation.—(1.) By the direct action of chlorine, either (α) on *a metal* ($Mg+Cl_2=MgCl_2$) ; or (β) on *a basic oxide*, either in the cold (as AgCl), or when heated to redness, whereby the oxygen of the oxide is expelled ; or (γ) on *a heated mixture of carbon and a metallic oxide*, whereby carbonic oxide is evolved ($M'_2O+C+Cl_2=2M'Cl+CO$) ; or (δ) on *a sulphide*, whereby a chloride of sulphur and a metallic chloride are formed.

(2.) By dissolving a metal in aqua regia (this being in reality the action of nascent chlorine), evaporating the solution to dryness, and redissolving the residue in water (*e.g.*, Au, Pt, etc.).

(3.) By the action of hydrochloric acid gas, either (α) on *a metal* ($Na_2+2HCl=2NaCl+H_2$) ; or (β) on *an oxide* of a metal ($CuO+2HCl=CuCl_2+H_2O$) ; or (γ) on *a sulphide* of a metal.

(4.) By dissolving either a metal, or an oxide, hydrate, or carbonate of a metal in liquid hydrochloric acid, and evaporating. The hydrated chlorides may be prepared by this process. Many hydrated chlorides, however, evolve their chlorine as HCl, when their solutions are evaporated—

$$(MgCl_2 + H_2O = MgO + 2HCl).$$

(5.) The insoluble chlorides may be prepared by adding hydrochloric acid (or a soluble chloride) to a salt of the metal (*e.g.*, $AgCl$, $PbCl_2$, Hg_2Cl_2).

(6.) A chloride of a metal may sometimes be formed by treating the metal itself with the chloride of another metal, whereby the first metal will appropriate the chlorine of the second metal. Thus, if sodium be heated with magnesium chloride, sodium chloride and free magnesium are produced; or if potassium be heated with uranous chloride, potassium chloride and free uranium are formed. (Similarly, $SnCl_4$, $SbCl_3$, or $BiCl_3$ may be prepared by heating Sn, Sb, or Bi with $HgCl_2$.)

Varieties of Chlorides.—(1.) *Subchlorides* (M_2Cl_2); as *e.g.*, Mercurous chloride (Hg_2Cl_2), Cuprous chloride (Cu_2Cl_2).

(2.) *Monochlorides* ($M'Cl$ as KCl); *Dichlorides* ($M''Cl_2$ as $Ca''Cl_2$); *Trichlorides* ($M'''Cl_3$ as $Sb'''Cl_3$); *Tetrachlorides* ($M^{iv}Cl_4$ as $Pt^{iv}Cl_4$); *Pentachlorides* ($M^{v}Cl_5$ as $Sb^{v}Cl_5$); *Hexachlorides* ($M^{vi}Cl_6$ as $Mo^{vi}Cl_6$).

(3.) *Sesquichlorides* ($('M''')_2Cl_6$); as Ferric chloride (Fe_2Cl_6).

One metal is often found to combine with chlorine in more than one proportion. Thus—

(α.) $FeCl_2$ Ferrous chloride; and Fe_2Cl_6, Ferric chloride.

(β.) $PtCl_2$, Platinous chloride; and $PtCl_4$, Platinic chloride.

Properties.—(α.) *Sensible and Physical.*—The *colors* of the chlorides are various; the alkaline chlorides are white. Their *taste* is mostly saline or bitter. Generally they have no odor. They usually crystallize in cubes, but sometimes in square prisms (Hg_2Cl_2), sometimes in rhombohedra ($CaCl_2$), and sometimes in oblique prisms ($BaCl_2$). Some chlorides are soft, as argentic chloride (horn silver), and those chlorides known as *metallic butters* ($SbCl_3$; $SnCl_2$); whilst some are liquid, and are known as *metallic oils* ($SbCl_5$; $AsCl_3$). When exposed to the air they are mostly deliquescent.

Action of Heat.—(i.) They are all fusible and volatile. (1.) Some volatilize at about 212° F. (100° C.); *e.g.*, Al_2Cl_6, Fe_2Cl_6, $AsCl_3$, etc.; (2.) some at a red heat, *e.g.*, $NiCl_2$; (3.) but most of them at a higher temperature.

(ii.) Some are *partly* decomposed by heat. Thus $2CuCl_2$ becomes, at a red heat, $Cu_2Cl_2 + Cl_2$.

(iii.) Some are *completely* decomposed by heat; as, *e.g.*, $PtCl_4$, $PdCl_2$, $AuCl_3$.

(iv.) Many (the chlorides of the noble metals excepted) when *ignited in air or oxygen* are decomposed, with the formation of an oxide and the escape of chlorine.

(v.) Many (the chlorides of the alkaline metals and those of barium and mercury excepted) when *heated in the presence of water,* form oxides and hydrochloric acid. [N.B. Bismuth forms an oxychloride.]

(vi.) All (excepting the chlorides of the alkalies and alkaline earths) when *ignited in a free current of hydrogen* are decomposed, hydrochloric acid being formed.

Solubility in Water.—The chlorides are generally deliquescent, and very soluble in water. $PbCl_2$ is, however, only very slightly soluble, whilst AgCl, Hg_2Cl_2, AuCl, and $PtCl_2$ are insoluble.

Solubility in Alcohol and Ether.—Most chlorides are very soluble in alcohol, but NaCl is only slightly soluble, and some others, as KCl, $BaCl_2$, AgCl, and Hg_2Cl_2 are insoluble. Excepting those of the noble metals, the chlorides are insoluble in ether.

Action of Light.—Some chlorides, as, *e.g.*, AgCl, are decomposed by exposure to light.

Action of Electricity.—The chlorides are mostly decomposed by electricity.

(*β*.) *Chemical.*—The chlorides have generally an acid, but never an alkaline reaction. The chlorides of the alkaline metals are neutral.

Water dissolves most chlorides without decomposition, but there are certain exceptions, such, *e.g.*, as $SbCl_3$, $BiCl_3$, $SnCl_2$, which form hydrochloric acid and an oxychloride when treated with water ($BiCl_3+H_2O=2HCl+BiClO$).

Acids, especially when heated, decompose the chlorides (argentic and mercurous chlorides excepted), setting free hydrochloric acid. All the soluble chlorides, when heated with sulphuric acid and manganese dioxide, evolve chlorine, which is also commonly given off when they are heated with nitric acid. The chlorides of the metals combine amongst themselves ($2KCl,PtCl_4$), also with the chlorides of the non-metals (KCl,ICl_3) to form double chlorides, and also with metallic oxides, to form oxy-chlorides ($3HgO,HgCl_2$).

Tests.—(1.) *For the soluble chlorides :—*

(*a*.) *Argentic nitrate :* a white precipitate of AgCl, insoluble in nitric acid, soluble in ammonia, in potassic cyanide, and in sodium thiosulphate. The precipitate of AgCl, blackens on exposure to light.

(*β*.) *Mercurous nitrate :* a white precipitate of mercurous chloride (calomel) [$Hg_2(NO_3)_2+2NaCl=2NaNO_3+Hg_2Cl_2$] soluble in chlorine water, and blackened by ammonia.

(*γ*.) *Plumbic acetate ;* in strong solutions, a white crystalline precipitate of plumbic chloride ($PbCl_2$), soluble in excess of water.

(2.) *For the insoluble chlorides* (AgCl, Hg_2Cl_2, $PbCl_2$) :—

Boil the insoluble chloride in a pure solution of potassic hydrate, filter off the undissolved oxide, acidulate the solution with nitric acid, and test with argentic nitrate for chlorine.

[Note.—$PbCl_2$ is readily soluble in *boiling* water.]

Estimation of Chlorides.—100 grains of AgCl=24·74 of chlorine.

Uses.—Common salt in diet, etc. Mercury and other chlorides are used in medicine.

III. Iodides.

Definition.—Compounds of metals with iodine (the radical of HI).

Natural History.—The iodides are found in all three kingdoms of nature, but chiefly in sea and in mineral waters, and in the plants and animals living therein. Argentic iodide is a natural mineral.

Preparation.—1. (*a.*) By the direct union of iodine and the metal (*e.g.*, HgI_2, AsI_3, BiI_3, Hg_2I_2, Al_2I_6, SnI_4); or (*β*) by passing iodine vapor over metallic oxides, either alone or mixed with carbon.

2. By the action of hydriodic acid on metals (Hg), or on the oxides, hydrates, and certain salts (as AgCl) of the metals.

3. By the action of iodine on a solution of the alkalies and alkaline earths, whereby an iodide and an iodate are formed, the iodate on ignition becoming an iodide (Process of P.B. for making KI).

4. The insoluble iodides may be prepared by adding a metallic salt to a solution of potassium iodide (HgI_2, AgI, PbI_2, SnI_2).

Properties.—The iodides are closely allied to the chlorides.

(*a.*) *Sensible and Physical.* The alkaline iodides are white, but the remainder (as HgI_2, PbI_2, etc.), are generally colored. They commonly crystallize in cubes. They are mostly soluble both in alcohol and in water; but Hg_2I_2, HgI_2, AgI, BiI_3, PdI_2, are insoluble in water, and PbI_2 is but very slightly soluble.

Action of Heat. The iodides are less fusible and less volatile than the corresponding chlorides:—

(1.) Most iodides are fusible, and many are volatile at a high temperature.

(2.) When *ignited in air or oxygen* they are usually decomposed, iodine being set free and an oxide of the metal formed (Exceptions—KI, NaI, PbI_2, BiI_3). In the case of AuI_3, AgI, PtI_4, PdI_2, the metal is reduced and iodine set free.

(3.) When *heated in the presence of water*, they are mostly decomposed into hydriodic acid and an oxide of the metal.

Light acts on many of the iodides. Thus AgI is blackened; Hg_2I_2 is decomposed into Hg and HgI_2.

(*β.*) *Chemical.* The iodides are decomposed (1) by *chlorine* and *bromine*, iodine being set free; (2) by *hydrochloric acid*, hydriodic acid and a chloride of the metal being formed; (3) by *sulphuric, nitric and nitrous acids*, and (4) by being heated with sulphuric acid and manganese dioxide, when iodine is evolved. The iodides of those metals which form acids with oxygen, viz., SnI_4, SbI_3, TeI_4, AsI_3, are decomposed by water, and an oxide of the metal precipitated.

The iodides readily combine amongst themselves; also with oxides, forming *oxy-iodides* (such as SbIO and BiIO, formed by the action of water on SbI_3 and BiI_3 respectively), and with chlorides (SnI_2SnCl_4). Moreover, the metallic iodides absorb ammonia in definite proportions.

Tests for Iodides—(1.) *Starch water* (a trace either of chlorine water or of nitric or sulphuric acid to liberate the iodine being added), gives, with a soluble iodide, the ***blue iodide of starch.***

(2.) *Mercuric chloride* ($HgCl_2$), a scarlet ppt. of *mercuric iodide* (HgI_2) soluble in excess both of the iodide and of the test solution.

(3.) *Plumbic acetate,* a yellow ppt. of *plumbic iodide* (PbI_2), soluble in hot water, and precipitated in yellow crystalline scales on cooling.

(4.) *Argentic nitrate,* a buff ppt. of *argentic iodide* (AgI), insoluble in nitric acid, very sparingly soluble in ammonia, soluble in potassic cyanide.

(5.) *A mixture of cupric sulphate and ferrous sulphate,* a white ppt. of *cuprous iodide* (Cu_2I_2). ($2CuSO_4+2FeSO_4+2KI=Cu_2I_2+K_2SO_4+Fe_23SO_4$).

(6.) *Salts of Palladium,* a brown ppt. of *Palladious iodide* (PbI_2), insoluble in water. (The $PdCl_2$ is freely soluble.)

Estimation.—If chlorides and bromides be absent, the iodide may be estimated as AgI (100 grs.=54·04 I); but if chlorides and bromides be present, it must be precipitated as PdI_2 (100 grs.=70·457 I).

Uses.—In *medicine.* KI (a solution of which is used as a solvent for iodine), CdI_2 or FeI_2 (prepared by direct union), PbI_2 (prepared by the action of KI on $Pb2NO_3$), and S_2I_2 are officinal.

IV.—Bromides.

Definition.—Compounds of metals, etc., with bromine.

Natural History.—Bromides are found in sea-water and in saline springs. Argentic bromide occurs as a natural mineral.

Preparation.—Their preparation corresponds to that of the iodides:—

(1.) By the direct union of a metal with bromine ($SnBr_4$).

(2.) By the action of hydrobromic acid on a metal ($SnBr_2$) or on the carbonate ($BaBr_2$), or soluble salt (Hg_2Br_2) of the metal.

(3.) By the action of bromine, dissolved in CS_2, on an oxide ($AsBr_3$).

(4.) Mercurous bromide. By the action of mercury on mercuric bromide, and afterwards subliming.

Varieties.—These correspond to the chlorides.

Properties.—(*a.*) *Physical.*—They are all solid. They may all be fused and volatilized, excepting $AuBr_3$ and $PtBr_4$, which are decomposed by heat. They are nearly all soluble in water, $AgBr_2$, Hg_2Br_2, and $PbBr_2$ being the least soluble.

(*β.*) *Chemical.*—Heated in chlorine, the bromides are decomposed and undergo conversion into chlorides, bromine being liberated. Heated with hydrochloric acid, hydrobromic acid is evolved. They are all decomposed by sulphuric and nitric acids, hydrobromic acid being set free, which is itself decomposed if the sulphuric or the nitric acid be in great excess, when free bromine is evolved, together with SO_2 or NO_2. By the joint action of sulphuric acid and manganese peroxide, the bromides evolve free bromine. The bromides combine amongst themselves and with sulphides, as well as with oxides to form oxybromides (such as SbBrO and BiBrO, antimonious or bismuthous oxybromides, formed by the action of water on $SbBr_3$ or $BiBr_3$). They also absorb ammonia freely.

Tests for Bromides.—(1.) Add to the solution of a bromide a little *chlorine water* or a *few bubbles of chlorine* (avoiding excess). The liquid becomes red from bromine being set free. Divide this into two parts (α and β) :—

(α.) *Shake up one part with ether or with carbon disulphide,* by which means the bromine may be dissolved out of the solution.

(β.) *Add starch water,* when the yellow bromide of starch will be formed.

(2.) *Argentic nitrate;* a whitish-yellow ppt. of *argentic bromide* (AgBr), insoluble in hot nitric acid, sparingly soluble in ammonia.

(3.) *Mercurous nitrate* ($(Hg_2)''2NO_3$) ; a yellowish-white ppt. of *mercurous bromide* (Hg_2Br_2), soluble in chlorine water, bromine being set free.

(4.) *Plumbic acetate;* a white ppt. of *plumbic bromide* ($PbBr_2$), less soluble in water than $PbCl_2$. Soluble in dilute nitric acid.

(5.) *Palladium nitrate* (*in solutions not containing chlorides*); a black ppt. of *palladium bromide.*

Estimation of Bromides.—In the absence of chlorides and iodides, the bromine may be estimated as AgBr (100=42·55 Br).

Uses.—Chiefly in *medicine.* NH_4Br (prepared by the action of HBr on NH_3), $FeBr_2$ (prepared by direct union), KBr (prepared as KI), are officinal.

V.—Fluorides.

Definition.—Compounds of metals, etc., with fluorine.

Natural History.—The fluorides are abundant in the mineral kingdom, and are also found in animals and vegetables.

Preparation.—(1.) By the action of hydrofluoric acid or of calcic fluoride and hydrochloric acid on a metal, its oxide or carbonate, etc. (SnF_2, ZrF_4, AsF_3, SbF_3, BiF_3).

(2.) The insoluble fluorides may be prepared by mixing a solution of a salt of the metal with a solution of potassium or sodium fluoride.

Properties.—(a.) *Physical.* They are mostly solid, and crystallise in cubes. Silicic fluoride (SiF_4) is a gas.

Action of Heat.—All the fluorides fuse by heat (*fluo,* to flow). Many, such as SbF_3, AsF_3, Cr_2F_6, HgF_2, SnF_4, ZnF_2, ZrF_4, are volatile. They are not decomposed, either when ignited alone or with carbon.

Action of Water.—A few fluorides are freely soluble in water (as AgF, SnF_4), their solutions corroding glass; some are sparingly soluble (as KF, NaF, Fe_2F_6), but the majority are insoluble. AsF_3 is decomposed by water. Antimonious fluoride (SbF_3) forms, on the addition of water SbOF.

(β.) *Chemical.*—The fluorides of ammonium, sodium, and potassium have an alkaline reaction. When ignited in a current of steam they form oxides of the metals and hydrofluoric acid. When ignited in a current of chlorine many of them are decomposed, and a chloride of the metal produced.

The fluorides are not readily acted on by nitric acid. With sulphuric acid they evolve hydrofluoric acid, leaving a metallic sulphate. They exhibit a marked tendency to combine amongst themselves, as $SnF_4,2KF$ (called a *stannico-fluoride*, corresponding to and isomorphous with the silico-fluorides), or $ZrF_4,2KF$ (called *zircono-fluorides*), or $ThF_4,2KF$ (called *thoro-fluorides*), or $NbF_5,2KF$ (called *niobo-fluorides*), or $SiF_4,2KF$ (called *silico-fluorides*, or *fluosilicates*). They also combine with another molecule of the acid (HF, KF).

Tests.—(1.) The *fluorides* give precipitates with salts of lead, barium, and magnesium, but no precipitate with nitrate of silver.

(2.) *A salt of calcium* gives an almost invisible jelly-like precipitate of CaF_2, rendered more apparent on the addition of ammonia. The precipitate is not very soluble in acids, but when treated with sulphuric acid, fluorine is evolved, which acts on glass.

Estimation of Fluorides.—Mix the fluorides with powdered glass and sulphuric acid, and distil into an ammonia solution. The SiF_4 which comes over is decomposed by the water. Evaporate the contents of the receiver to dryness, by which means the silica will be rendered insoluble. Dissolve out the ammonium fluoride with water, and weigh the silica. (Wilson.)

Uses.—Chiefly for glass etching.

VI.—Sulphides (SULPHURETS).

Definition.—Compounds of metals, etc., with sulphur.

Natural History.—Found largely in the mineral kingdom.

Preparation.—(1.) By the direct union of sulphur with a metal (such as CuS, FeS, PbS, SnS), or with a metallic oxide. In this latter case, however, a variable proportion of sulphate is formed simultaneously with a sulphide.

(2.) By heating a metallic oxide in a current of H_2S or CS_2 vapor. In this way titanium sulphide may be prepared from titanic anhydride ($TiO_2+CS_2=TiS_2+CO_2$).

(3.) By the ignition (reduction) of *sulphates,* either (*α*) with *carbon* or with an organic substance (as, *e.g.*, in the preparation of sulphides of the alkalies and alkaline earths) when CO is evolved ($K_2SO_4+4C=K_2S+4CO$) ; or (*β*) in *a current of hydrogen,* as, *e.g.*, in the preparation of the protosulphides of the alkalies, and the subsulphides of other metals, when some of the sulphur volatilizes.

(4.) By the precipitation of metallic solutions, either (*α*) by *sulphuretted hydrogen,* the solution of the salt of the metal being acid in the case of the formation of Sb_2S_3, SnS_2, As_2S_3, Au_2S_3, PtS_2; or either acid or neutral in the case of PbS, HgS, Ag_2S, Bi_2S_3, CuS, CdS: or, (*β*.) By an *alkaline sulphide, e.g.*, ZnS, MnS, etc.

FORMATION OF SULPHIDES BY H_2S.

Class I.—*Metals not precipitated by* H_2S, *their sulphides being soluble in water.**
Examples (K, Na, Li, Ba, Sr, Ca, Mg).

Class II.—*Metals precipitated by* H_2S *in an* ACID *solution, but not in an* ALKALINE *solution,* their sulphides forming double and soluble salts, with the alkalies.
Hence: *they are soluble in, and not precipitated by, an excess of ammonium sulphide.*
Examples (Sb, Sn, As, Au, Pt).

Class III.—*Metals precipitated by* H_2S *in an* ALKALINE *solution, but not in an* ACID *solution,* the acid dissolving the sulphide. They do not form double compounds with the alkalies.
Hence: *they are insoluble in, and precipitated by, ammonium sulphide.*
Examples (Ni, Co, Zn, Mn, Fe).

Class IV.—*Metals precipitated by alkaline sulphides as oxides, and not as sulphides.*
Examples (Cr, Al).

Class V.—*Metals precipitated by* H_2S, *both in an acid and alkaline solution.*
Hence: *they are precipitated equally by* H_2S, *and ammonic sulphide.*
Examples (Pb, Hg, Ag, Bi, Cu, Cd).

Properties.—(*α*.) *Physical.*—All metallic sulphides are solid, and many are crystalline (cubic). They are of various colors ; thus, ZnS is *white;* MnS is *flesh red;* CdS, As_2S_3, SnS_2, are *yellow;* SnS is *chocolate;* whilst the rest are more or less black. Many have a metallic lustre. The sulphides of the alkali metal and those of barium and strontium are freely soluble in water ; calcium and magnesium sulphides are slightly soluble, whilst the rest are insoluble. They are generally fusible and volatile. The further action of heat upon them will be studied under the next head, "Chemical Properties."

(*β*.) *Chemical.*—There is a close relationship between the oxides and the sulphides. As oxygen often combines with a metal in more than one proportion, forming protoxides and peroxides, so sulphur forms protosulphides, as ferrous sulphide (FeS), and persulphides as ferric sulphide (Fe_2S_3). This law, however, is not absolute. There is no sulphide, *e.g.*, corresponding to MnO_2, and no oxides corresponding to K_2S_3 and K_2S_5 (?).

---

* Baudrimont (Journ. Pharmac. Chem., Series IV. xxii. 15-19) points out that a 40° Baumé solution of sodic, and probably of potassic hydrate at 15° C., is precipitated by H_2S, the precipitate having the composition $Na_2S, 9H_2O$. It is very soluble in water.

Action of Air.—On exposure to air, even at common temperatures, some sulphides become sulphates ($CuS + O_4 = CuSO_4$), an action utilized in the separation of copper from tin. Some (*e.g.*, those metallic sulphides which form alkaline oxides), when exposed to moist air, yield, in the first instance, a mixture of an oxide with a bisulphide, and afterwards of an oxide with a thiosulphate, this latter being formed by the further oxidation of the bisulphide. Thus—

(α.) $4Na_2S + O_2 = 2Na_2O + 2Na_2S_2$.
Sodium sulphide + Oxygen = Sodium oxide + Sodium bisulphide.

(β.) $2Na_2S_2 + 3O_2 = 2Na_2S_2O_3$.
Sodium bisulphide + Oxygen = Sodium thiosulphate.

Some sulphides, when exposed to the air, part with their sulphur and become oxides. In this way the spent oxide of gas-works is "revivified." Thus—

$4FeS + 3O_2 = 2Fe_2O_3 + 2S_2$.
Ferrous sulphide + Oxygen = Ferric oxide + Sulphur.

Some sulphides combine with oxides to form *oxy-sulphides* ($Sb_2O_32Sb_2S_3$), and some with carbon disulphide to form *sulpho-carbonates* (K_2S,CS_2).

Action of Heat.—(α.) The protosulphides, if air be excluded, are not decomposed by heat.

(β.) Heated in the presence of air, some sulphides are *partially decomposed*, as, *e.g.*, FeS_2 becomes FeS. Some are *changed into sulphates*, as, *e.g.*, in the formation of zinc sulphate from blende ($ZnS + 2O_2 = ZnSO_4$). In some the sulphur is expelled as sulphurous anhydride, and *an oxide of the metal formed*, as, *e.g.*, in extracting copper from the ore ($Cu_2S + 2O_2 = 2CuO + SO_2$). In some cases *the metal is entirely reduced*, as, *e.g.*, Au_2S_3, PtS_2; whilst in others a mixture of the reduced metal with a sulphate is formed (Ag).

(γ.) Some sulphides sublime when heated, as, *e.g.*, As_2S_3 (*orpiment*), and HgS (*cinnabar*).

(δ.) Some sulphides are reduced when *heated in a stream of hydrogen*, as, *e.g.*, Ag_2S, CuS, Bi_2S_3, SnS_2, Sb_2S_3.

(ε.) Some sulphides are reduced when *heated with iron*, as, *e.g.*, PbS, SnS_2.

(ζ.) All sulphides are decomposed when *heated in a stream of chlorine*, chloride of sulphur and a chloride of the metal being formed.

Action of Acids.—Cold dilute sulphuric acid and also hydrochloric acid dissolve most of the sulphides, sulphuretted hydrogen being evolved. With HCl a chloride of the metal is formed ($Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$.) The sulphides of cobalt, of nickel, and of platinum are not acted upon by hydrochloric acid unless the sulphides be boiled in the acid. All sulphides (excepting mercuric sulphide) are decomposed by nitric acid, sulphuric acid and a nitrate of the metal being formed. They are all freely attacked by nitro-hydrochloric acid.

Action of Sulphuretted Hydrogen. Sulph-hydrates.—When sulphuretted hydrogen is passed through a solution of the sulphide of an alkali metal or of an alkaline earth metal, soluble *sulph-hydrates, hydrosulphides* or *hydric-sulphides*, as they are called, are formed ($K_2S + H_2S = 2KHS$). This compound holds an intermediate position between sulphuretted hydrogen and the ordinary sulphide, and closely corresponds in constitution to a hydrate. The ammonium hydric-sulphide (NH_4HS) belongs to this class. The sulph-hydrates smell of sulphuretted hydrogen, the gas being set free when they are acted upon by a metallic salt, a reaction serving to distinguish them from simple sulphides ($2NH_4HS + MnSO_4 = (H_4N)_2SO_4 + MnS + H_2S$).

Sulphides (like oxides) are both basic and acid. Thus, an acid sulphide (as As_2S_5) may react on a basic sulphide (as Na_2S) to form a new and double compound, such as ($3Na_2S,As_2S_5$.) Most of these double sulphides are soluble in water. The importance of this fact in analysis is manifest, inasmuch as we are often able in a mixed precipitate of metallic sulphides, to dissolve out one sulphide by the addition of a sulphide of an alkali metal (as NH_4HS).

Action of Alkalies and Alkaline Carbonates.—The sulphides are decomposed by fusion with alkaline carbonates or with hydrated alkalies.

Tests for the Sulphides :—

(1.) Heated with the blowpipe they emit an odor of SO_2.

(2.) Moistened with HCl they evolve H_2S, which blackens lead paper.

(3.) *Sodium nitro-prusside* gives a purple color with a neutral or alkaline solution of a sulphide.

Estimation of Sulphides :—

(1.) By first oxidizing the sulphur to sulphuric acid by aqua regia or chlorine, and afterwards precipitating the sulphuric acid as $BaSO_4$ ($100\ BaSO_4 = 13{\cdot}73$ of S.).

(2.) To determine the quantity of free H_2S or of a soluble sulphide present in solution, mix the solution with a little starch water and acidulate with acetic acid ; add to this a standard solution of iodine in potassium iodide, until the blue iodide of starch is formed.

The H_2S converts the iodide into HI, whilst sulphur is set free ($2H_2S + 2I_2 = 4HI + S_2$).

VII.—Nitrides.

Definition.—Compounds of a metal with nitrogen.

Examples.—Magnesium nitride (Mg_3N_2), mercuric nitride (Hg''_3N_2), copper nitride (Cu_6N_2), chromium nitride (CrN).

Preparation.—(1.) By heating the metal (Mg ; Cr) or an oxide of the metal (Hg_3N_2 ; Cu_6N_2) in nitrogen.

(2.) By the action of gaseous ammonia on the chloride (CrN).

Properties.—Certain of the nitrides are decomposed by moisture ($Mg_3N_2 + 3H_2O = 2NH_3 + 3MgO$). They all undergo decomposition by heat, and frequently with explosive violence.

VIII.—Arsenides.

Definition.—Compounds of a metal with arsenicum (As), such as copper arsenide (Cu_6As_2), which is found native.

IX. and X.—Selenides and Tellurides.

Definition.—Compounds of metals with selenium or tellurium.

These compounds are closely allied to sulphides.

The presence of selenium may be known by the peculiar smell emitted, when the selenide is heated in the reducing flame of the blowpipe.

XI.—Phosphides.

Definition.—Compounds of metals with phosphorus.

Natural History.—The phosphides are never met with native.

Preparation.—In one or other of the following ways :—

(1.) By the direct union of phosphorus with a metal under petroleum (Au, Pt, Ca).

(2.) By igniting a metal with a mixture of phosphoric anhydride (or a phosphate) and carbon.

(3.) By passing the vapor of phosphorus over lime.

(4.) By passing phosphoretted hydrogen through a solution of a metallic salt or over a chloride (*e.g.*, Cu).

Properties.—The phosphides are brittle solids, with a metallic lustre. They are decomposed by heat, especially in the presence of air, with the formation either of a phosphate or of phosphoric anhydride and the free metal. The phosphides of the alkalies and of the alkaline earths decompose water, generating self-inflammable phosphoretted hydrogen.

XII.—Carbides.

Definition.—Compounds of metals with carbon.

The carbides of iron are the only ones of importance. Manganese, palladium, etc., also form carbides. The carbides are usually more fusible than the metals.

XIII. and XIV.—Silicides and Borides.

Definition.—Compounds of metals with silicon and boron.

A boride of magnesium (Mg_3B_2), may be prepared by heating the metal with amorphous boron in a closed crucible.

The **Cyanides** will be considered under Cyanogen.

XV.—Hydrides.

Definition. — Compounds of a metal with hydrogen. Only six metals form true hydrides, although many other metals mechanically absorb hydrogen.

Preparation.—(1.) By heating the metal in a current of hydrogen (K_4H_2, Na_4H_2, Pd_4H_2).

(2.) By the reducing action of hypophosphorous acid on a sulphate (Cu_2H_2).

(3.) By electrolysis; using the metal as the negative electrode (Pd_4H_2).

Illustrations of the metals that form hydrides:—

Potassium	(K_4H_2)	A crystalline mass; inflames spontaneously in air. Dissociation commences at 752° F. (400° C.) in a hydrogen atmosphere at normal pressure, and at 392° F. (200° C.) in vacuo.
Sodium	(Na_4H_2)	Sp. gr. 0·959. More permanent than K_4H_2. Dissociates in hydrogen at 420° C., and in vacuo at 788° F. (300° C.).
Copper	(Cu_2H_2)	A liquid. Decomposes at 140° F. (60° C.) Inflames spontaneously in chlorine.
Palladium	(Pd_4H_2)	(*See* Palladium.)
Arsenicum	(AsH_3)	(*See* Arsenicum.) A gas. A solid hydride of arsenicum is believed to exist.
Antimony......	(SbH_3)	(*See* Antimony.)

OXYSALTS.

Definition.—Salts formed from an oxygen acid, by the displacement of a part or all of its hydrogen by a metal, or its equivalent.

I.—Sulphates.

Definition.—Salts formed from sulphuric acid (H_2SO_4).

Natural History.—The sulphates are found in the animal, vegetable, and mineral kingdoms.

Varieties and Constitution.—(*a.*) *Normal Sulphates* (M'_2SO_4). Sulphates where all the displaceable hydrogen of the H_2SO_4 is exchanged for a metal, etc. (as K_2SO_4, $Ba''SO_4$, $Pb''SO_4$, etc.).

(*β.*) *Acid Sulphates* ($M'HSO_4$). Sulphates where the displaceable hydrogen of the H_2SO_4 is only partially exchanged for a metal, etc., (as $HNaSO_4$, hydric sodic sulphate, also called bisulphate).

(γ.) *Basic Sulphates.* Sulphates where the base present is in excess of the acid, (as, *e.g.*, Hg''_3SO_6, or $HgSO_4.2HgO$, turpeth mineral).

(δ.) *Double Sulphates* are formed by the combination of two sulphates, as, *e.g.*, in the alums ($K_2SO_4,Al_23SO_4+24\,Aq.$).

Many sulphates are anhydrous (Ba, Sr, Pb, Ag); some contain 5 molecules of water (Cu); most contain 7 molecules (Mg, Zn, Fe, Co); and some 10 molecules (Na). The alums contain from 12 to 27 molecules.

Preparation.—(1.) By the artificial or spontaneous oxidation of sulphides. Thus FeS and CuS, by roasting or by exposure to weather, become $FeSO_4$ and $CuSO_4$.

(2.) By the action of sulphuric acid on a metal, or an oxide, carbonate, or other salt of a metal:—

(α.) The action of a *dilute acid* on metals is accompanied with the evolution of hydrogen (*e.g.*, $Zn+H_2SO_4=ZnSO_4+H_2$).

(β.) The action of a *concentrated acid* and *heat* on the metals is accompanied with the evolution of sulphurous anhydride (*e.g.*, Cu, Ag, Sb, Sn, Hg); ($Cu+2H_2SO_4=CuSO_4+2H_2O+SO_2$).

(γ.) Action on *oxides* (*e.g.*, $ZnO + H_2SO_4=ZnSO_4+ H_2O$; —$2MnO_2+2H_2SO_4=2MnSO_4+2H_2O+O_2$).

(δ.) Action on *sulphides* (*e.g.*, $FeS+H_2SO_4=FeSO_4+H_2S$).

(ε.) Action on *hydrates* (*e.g.*, $MnH_2O_2+H_2SO_4=MnSO_4+2H_2O$).

(ζ.) Action on *carbonates*, (*e.g.* $Na_2CO_3+H_2SO_4=Na_2SO_4+H_2O+CO_2$).

(η.) Action on *chlorides* (*e.g.*, $2NaCl+H_2SO_4=Na_2SO_4+2HCl$).

(N.B.—Sulphuric acid displaces all acids that boil at a lower temperature than itself).

(3.) By the action of sulphurous anhydride on metallic peroxides—($SO_2+PbO_2=PbSO_4$).

(4.) The insoluble sulphates are formed by adding a soluble sulphate to a soluble salt of the metal. Thus—($BaCl_2 + H_2SO_4 = BaSO_4 +2HCl$).

(N.B.—The sulphates often occur as residues in the preparation of volatile acids. Thus K_2SO_4 is obtained in the nitric acid, and Na_2SO_4 in the hydrochloric acid manufacture.)

Properties.—(α.) PHYSICAL.—The sulphates are all crystallizable solids. The crystals are of different shapes; viz., *cubic*, as in the alums; *singly oblique*, as in the sulphates of sodium, iron, and cobalt, and in the non-aluminous double sulphates; *doubly oblique*, as in the sulphates of copper and manganese. They are generally white, but some few are colored. Their taste is usually a saline-bitter and astringent. They have no odor.

Action of Heat.—(i.) The normal sulphates of the alkalies and of the alkaline earths, and plumbic sulphate, are not decomposed by heat.

(iii.) The sulphates of Mg, Mn, Zn, Cd, Ni, Co, and Cu are decomposed by an intense heat, SO_2 and O being evolved ($CuSO_4 = CuO + SO_2 + O$). (Thus, $ZnSO_4$ has been suggested as a source of oxygen.)

(iii.) The remaining sulphates are easily decomposed when heated, sulphuric anhydride being evolved in the case of the sulphates of the noble metals, and sulphurous and sulphuric anhydrides in the remainder ($2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$).

The sulphates are mostly soluble in water, and many soluble in alcohol.

(β.) CHEMICAL.—All the sulphates redden litmus, except the normal sulphates of the alkalies and alkaline earths.

Heated with carbon or with hydrogen, they may all be decomposed. Different reactions occur as follows :—

(i.) In some cases, as with the sulphates of the alkalies and alkaline earths, a sulphide is formed, CO, H_2O, or H_2S being evolved* ($K_2SO_4 + C_4 = K_2S + 4CO$; $K_2SO_4 + 4H_2 = K_2S + 4H_2O$).

(ii.) Sometimes an oxide is formed (Mg, Zn).

(iii.) Sometimes an oxy-sulphide is formed (Sb, Mn).

(iv.) Sometimes the metal is reduced (Cu, Hg, Bi, Ag, and the noble metals).

[Note that in those cases where a sulphide is formed from a sulphate by heating with carbon (*e.g*, $BaSO_4 + 4C = BaS + 4CO$), the presence of the sulphide may be known by moistening the resulting sulphide with HCl, and testing for H_2S with lead paper.]

Action of Acids.—*Nitric acid* and *hydrochloric acid* act on the neutral alkaline sulphates, forming acid sulphates and chlorides respectively. The *fixed acids*, such as boric acid and phosphoric acid, when fused with the sulphates, decompose them, liberating sulphuric anhydride (*see* page 6).

Action of Water.—The sulphates generally are soluble in water, but—

(i.) The basic sulphates, with $BaSO_4$, $PbSO_4$. and $Sn2SO_4$ are insoluble.

(ii.) $SrSO_4$, $CaSO_4$, Ag_2SO_4 are nearly insoluble.

(iii.) $HgSO_4$ is decomposed by the action of water into "turpeth mineral" ($2HgO,HgSO_4$), a similar result occurring in the case of the sulphates of bismuth and antimony.

---

* NOTE.—In waters containing calcium sulphate and organic matter, a calcium sulphide is formed even at ordinary temperatures, by the reducing action of the organic matter on the sulphate. The sulphide is decomposed by the carbonic acid, H_2S being set free, which imparts to the water an unpleasant taste.

All the insoluble sulphates are decomposed when boiled in a solution of sodium carbonate, a soluble sulphate and an insoluble carbonate being formed.

Organic matter also decomposes the sulphates.

Tests and Estimation of Sulphates.—(A.) *Soluble sulphates:*—

(1.) A *soluble barium salt;* a white ppt. of $BaSO_4$, insoluble in nitric acid. 100 grs. $BaSO_4$=42grsH_2SO_4.

(2.) A *soluble lead or lime salt;* a white ppt. of $PbSO_4$ or $CaSO_4$.

(B.) *Insoluble sulphates:*—

(1.) Fuse the sulphate with a mixture of sodium and potassium carbonates, digest the residue with water, and test the filtrate for a soluble sulphate with $BaCl_2$.

Or, (2.) Boil the sulphate in a solution of sodium carbonate, and test the filtrate for a soluble sulphate.

Or, (3.) Fuse the insoluble sulphate, mixed with charcoal and sodium carbonate, on charcoal with the blow-pipe. Touch the residue formed with a drop of acid, when H_2S will be evolved from the sulphide.

Uses.—Plaster of Paris ($CaSO_4$) is used in the arts. The sulphates are largely used in medicine, especially *Epsom salts* ($MgSO_4,7H_2O$). *Glauber's salts* (Na_2SO_4, $10H_2O$); *Ferrous sulphate* or *green vitriol* ($FeSO_4,7H_2O$); *Zinc sulphate* or *white vitriol* ($ZnSO_4 7H_2O$).

ALLIES OF THE SULPHATES.

Selenates (from *selenic acid*, H_2SeO_4); *Chromates* (from *chromic acid*, H_2CrO_4); *Manganates* (from *manganic acid*, H_2MnO_4); *Tungstates* (from *tungstic acid*, H_2WO_4); *Molybdates* (from *molybdic acid*, H_2MoO_4); *Tellurates* (from *telluric acid*, H_2TeO_4).

II.—Selenates.

Definition.—Salts formed from selenic acid (H_2SeO_4).

The selenates are isomorphous with and closely allied to the sulphates. They are decomposed when boiled with hydrochloric acid, chlorine being evolved and selenic acid liberated, which suffers immediate reduction to selenious acid, from a solution of which, sulphurous acid will precipitate reduced selenium.

Potassium selenate, K_2SeO_4 is prepared by fusing selenious anhydride with nitre. It resembles the sulphate in appearance, but may be distinguished from it by its reaction with HCl.

Tests.—(1.) Salts of *barium*, *strontium*, and *lead* give white ppts., insoluble in dilute nitric acid, of $BaSeO_4$, $SrSeO_4$, and $PbSeO_4$ respectively.

(2.) *Barium selenate* may be known from *barium sulphate* by the reaction mentioned above with hydrochloric acid, and also by its emitting the characteristic selenium odor when heated on charcoal with the blow pipe.

III.—Tellurates.

Definition.—Salts formed from telluric acid (H_2TeO_4). The tellurates are unstable salts. They give a black precipitate with sulphuretted hydrogen. When heated they evolve oxygen, a tellurite remaining.

Potassium and sodium tellurates (K_2TeO_4 or Na_2TeO_4, and $2KHTeO_4, 3H_2O$), are prepared by adding telluric acid to an alkaline carbonate.

IV.—Chromates.

Definition.—Salts formed from chromic acid (H_2CrO_4), which is only known as a solution of the anhydride CrO_3.

Normal (M'_2CrO_4), *acid* (such as $K_2Cr_2O_7$), and *basic* (such as $PbCrO_4,PbO$) chromates are known.

The acid salts are nearly always anhydrous, and correspond to the pyrosulphates.

Although we speak of acid chromates, we must observe that there is no acid chromate comparable with an acid sulphate. If, for example, normal potassium chromate (K_2CrO_4), be mixed with a solution of chromic acid, $KHCrO_4$ is not formed, or (at any rate if formed) is immediately and at ordinary temperatures converted into the normal dichromate and water ($2KHCrO_4 = K_2Cr_2O_7 + H_2O$), the soluble dichromates being again converted into normal chromates on the addition of a base ($K_2Cr_2O_7 + 2KHO = 2K_2CrO_4 + H_2O$).

The chromates are all more or less of a yellow or red color, and act as powerful oxidizing agents. They are mostly very soluble in dilute nitric acid, and more or less soluble in water, excepting lead chromate, $PbCrO_4$ (chrome yellow), argentic chromate, Ag_2CrO_4, and the basic chromates, which are insoluble. They are usually decomposed by heat. The green chromic hydrate ($Cr_2O_3,7H_2O$) is precipitated when the chromates are treated with ammonium sulphide (sulphuretted hydrogen being evolved), or with the caustic alkalies or their carbonates, in which, excepting in the case of ammonium carbonate, they are soluble in an excess.

Tests.—Solutions yellow when neutral, red when acid, the color becoming green when acted on by reducing agents, a chromic salt remaining in solution. (1.) (α.) Salts of *silver* a crimson ppt. (Ag_2CrO_4).

(β.) Salts of *barium* and *lead*, yellow ppts. ($BaCrO_4$; $PbCrO_4$).

(γ.) *Mercurous salts,* a brick-red ppt. (Hg_2CrO_4).

These precipitates are soluble in nitric acid, and insoluble in acetic acid.

(2.) Mix the dry chromate with an equal part of chloride of sodium, and add two or three drops of sulphuric acid in a test-tube. Apply heat, when chromyl-chloride (chloro-chromic acid, CrO_2Cl_2) is set free, and may be known by the red fumes that condense in the cool part of the tube.

(3.) The insoluble chromates must be ignited on platinum foil with a mixture of nitre and sodium carbonate, by which means a soluble alkaline chromate is obtained ($KNaCrO_4$). This residue is to be dissolved in water, neutralized with acetic acid, and tested with the reagents described above.

(4.) Chromates (and all chromium salts) impart an emerald green color (chromium borate) to the borax bead.

Certain bodies termed *chloro-chromates* (such as CrO_3,KCl) have been prepared.

V.—Manganates.

Definition.—Salts formed from the hypothetical acid called manganic acid (H_2MnO_4). It is noteworthy that even the anhydride (MnO_3) of this acid has not been prepared. Examples : K_2MnO_4 ; Na_2MnO_4 ; $BaMnO_4$.

Preparation.—By the action of heat, in air or oxygen, on a mixture of manganese peroxide with caustic potash, baryta, etc., according to the salt required.

Properties.—The manganates are colored and unstable salts. They are soluble in water containing a free alkali. In common water, however, and more particularly if it contains a trace of free acid (even of carbonic acid), the salt is decomposed into manganese dioxide and a permanganate ($3K_2MnO_4+2H_2O=2KMnO_4+MnO_2+4KHO$). A manganate solution is decomposed by boiling, the solid salt being also decomposed by heat with the evolution of oxygen. The manganates are decomposed by all acids ;—with sulphurous, phosphorous, and hypophosphorous acids they are reduced to manganous salts, whilst with sulphuric acid permanganates are formed. All organic matter (*e.g.*, a filter paper) deoxidizes them, setting free the brown manganic oxide (Mn_2O_3). The presence of alkalies renders the manganates more stable.

Uses.—The manganates are employed as disinfectants, owing to the readiness with which they yield oxygen to organic matter. "Condy's green disinfecting fluid," is a solution of sodium manganate (Na_2MnO_4) dissolved in potash. It turns red (a permanganate being formed) on the addition of an acid.

[*Permanganates.* (*See* Index.) Salts of permanganic acid, $HMnO_4$, *e.g.*, $KMnO_4$, $Ba(MnO_4)_2$].

VI.—Tungstates.

Definition.—Salts formed from tungstic acid (H_2WO_4). They resemble the salts of molybdic acid.

Tungstic acid forms both normal and acid salts. The normal salts are salts of the acid H_2WO_4. Many of the tungstates are of very complex constitution. They all redden litmus, and are all decomposed by hydrochloric acid, a hydrate of tungstic acid being precipitated (H_2WO_4,H_2O).

By combining the normal salts with varying proportions of the acid, certain *polytungstates* may be formed, whilst a further class of *metatungstates* are known which do not yield a precipitate with an acid, except after prolonged boiling.

Uses.—The common sodium tungstate, which is a sodium paratungstate ($Na_{10}W_{12}O_{41}28H_2O$) is prepared by roasting the mineral wolfram with soda ash, and extracting the fused mass with water. It is used by the calico-printers as a mordant, and also for the purpose of rendering fabrics uninflammable. Tungstate of barium has been used as a paint, in the place of white lead.

VII.—Molybdates.

Definition.—Salts formed from molybdic acid (H_2MoO_4). There are several hydrates of the oxide MoO_3 which form salts.

Normal and acid molybdates have been prepared. The alkaline molybdates are soluble.

Ammonium molybdate ($(NH_4)6Mo_7O_{24},4H_2O$) is used in the laboratory for the purpose of precipitating phosphoric acid. The solution must be first acidulated with nitric acid, and afterwards boiled. The precipitate, which is yellow and crystalline, is phospho-molybdate of ammonium, from which, by the action of aqua regia, a body having the composition $H_3PO_4,11MoO_3,12H_2O$ (*phospho-molybdic acid*), insoluble in nitric acid, but soluble in alkalies, may be obtained.

VIII.—Stannates.

Compounds of H_2SnO_3 (*see* Stannic Acid). Sodium stannate (tin-prepare liquor Na_2SnO_3) is used as a mordant in calico-printing. Certain *meta-stannates* (salts of meta-stannic acid) (such as $Na_2H_8Sn_5O_{15}$) and *sulpho-stannates, e.g.*, $Na_2SnS_3,7H_2O$, are known.

IX.—Thiosulphates (sometimes called Sulpho-Sulphates and Hyposulphites).

Definition.—Salts formed from thiosulphuric acid ($H_2S_2O_3$).

Examples.—Potassium ($2K_2S_2O_3$, $3H_2O$); sodium ($Na_2S_2O_3$, $5H_2O$);

ammonium $(3(NH_4)_2S_2O_3,H_2O)$; barium (BaS_2O_3,H_2O) ; strontium $(SrS_2O_3,5H_2O)$; calcium $(CaS_2O_3, 6H_2O)$.

Sodium thiosulphate (*hyposulphite*) $(Na_2S_2O_3)$, as it is called, and other thiosulphates may be prepared either (1) by digesting together sulphur and a sulphite $(Na_2SO_3 + S = Na_2S_2O_3)$, or (2) by passing SO_2 through a solution of a metallic sulphide. (3.) The ammonium salt $[3(NH_4)_2S_2O_5,H_2O]$ is formed by decomposing calcium thiosulphate with ammonic carbonate.

Sodium thiosulphate $(Na_2S_2O_3)$ is prepared commercially, by exposing either the refuse of alkali works (soda or tank waste), or the refuse lime of gasworks which contains calcium sulphide, to the air, whereby a calcium thiosulphate is obtained $(2CaS + 2O_2 = CaS_2O_3 + CaO)$. When a solution of this salt is precipitated with sodium carbonate, the soluble sodium thiosulphate is formed, and calcium carbonate is precipitated $(CaS_2O_3 + Na_2CO_3 = CaCo_3 + Na_2S_2O_3)$.

The thiosulphates have been called sulpho-sulphates, from being regarded as sulphates where a sulphur atom has displaced an oxygen atom (*e.g.*, $Na_2SO_4 = Na_2SSO_3$). The thiosulphates are all decomposed by heat and by acids, sulphurous acid being evolved.

Uses.—Sodium thiosulphate, is used for extracting argentic chloride from an ore. It is largely employed in photography, the alkaline thiosulphates being solvents of the insoluble silver salts, thereby forming the sweet-tasted argentic thiosulphate $(Ag_2S_2O_3)$, which, with any excess of sodium thiosulphate, forms the compound $NaAgS_2O_3$.

$2AgCl$	+	$Na_2S_2O_3$	=	$2NaCl$	+	$Ag_2S_2O_3$.
Argentic chloride	+	Sodic thiosulphate	=	Sodic chloride	+	Argentic thiosulphate.

[NOTE : The white silver chloride, *i.e.*, the salt unacted upon by light, is *entirely* soluble in $Na_2S_2O_3$. After the AgCl has been exposed to light it blackens, an argentic subchloride, Ag_2Cl, being formed with free chlorine. When this argentic subchloride (Ag_2Cl) is treated with a solution of a thiosulphate, it is decomposed into $AgCl + Ag$, the chloride being soluble in the thiosulphate solution, whilst the reduced metal remains undissolved.

Sodium thiosulphate is also used as an "*antichlor*" for removing the last traces of chlorine from bleached goods, a process known as *killing the bleach*." It is also used in medicine (hyposulphite of soda, B.P.).

Tests.—(1.) Soluble thiosulphates dissolve the insoluble argentic salts.

(2.) *Lead salts ;* white ppt. of lead thiosulphate (PbS_2O_3).

(3.) *Mercurous nitrate ;* black ppt. of mercurous sulphide (Hg_2S).

(4.) The thiosulphates decolorise an alcoholic solution of iodine.

(5.) A thiosulphate is decomposed by HCl, the thiosulphuric acid $(H_2S_2O_3)$ set free being instantly decomposed $(H_2S_2O_3 = H_2O + SO_2 + S)$.

X.—Sulphites (CLOSELY ALLIED TO CARBONATES).

Definition.—Salts formed from sulphurous acid (H_2SO_3). The acid is dibasic, forms both normal salts, such as Na_2SO_3, and acid salts, such as $NaHSO_3$.

Preparation.—By acting with sulphurous acid on the oxides or on the carbonates of metals, either in solution or in suspension in water.

Properties.—The sulphites are solid and inodorous salts. The alkaline sulphites are very soluble in common water, the sulphites of barium, strontium and calcium being also soluble in water containing free SO_2. In such solution the sulphites exist as acid salts. On evaporation, decomposition results with the formation of the normal salts and free SO_2. The remaining sulphites are difficult of solution.

When heated they are decomposed with the liberation of SO_2.

When treated with *sulphuric acid* or with *hydrochloric acid*, SO_2 is evolved. *Nitric acid* converts the sulphites into sulphates.

The sulphites, especially when moist, have a great affinity for oxygen, attracting it from the air. They act, therefore, as powerful reducing agents, changing ferrous to ferric salts, arsenic to arsenious acid; reducing chromic acid, and precipitating gold, etc., from solutions containing an excess of hydrochloric acid.

Tests.—(1.) A sulphite, when treated with hydrochloric or other strong acid, evolves SO_2 ($KSO_3 + 2HCl = 2KCl + SO_2 + H_2O$). Sulphurous acid is known by its action on paper moistened with starch and iodic acid. The iodic acid is reduced, the free iodine acting on the starch.

(2.) Add to a sulphite dissolved in a little water, a fragment of zinc and hydrochloric acid; H_2S (known by its blackening lead paper) will be evolved.

(3.) *Argentic nitrate;* a white ppt. of *argentic sulphite* ($AgSO_3$) soluble in excess of the sulphite. When boiled with water, the metal is partially reduced, and sulphuric acid formed ($AgSO_3 + H_2O = H_2SO_4 + Ag$).

(4.) *Barium nitrate;* a white ppt. of *barium sulphite, soluble in* HCl. If a few drops of chlorine water or of nitric acid be added to this solution, *barium sulphate* is formed, which is *insoluble in acids.*

Uses.—The sulphites are employed to check fermentation, and to prevent the growth of fungi. They are also used as "antichlors" to expel chlorine ($Na_2SO_3 + H_2O + Cl_2 = Na_2SO_4 + 2HCl$).

XII.—Selenites.

The salt K_2SeO_3 has been prepared.

XIII.—Dithionates (*See* page 189).

Definition.—Salts formed from dithionic acid $H_2S_2O_6$.

Examples.—Potassium ($K_2S_2O_6$) ; sodium ($Na_2S_2O_6,2H_2O$) ; lithium ($Li_2S_2O_6,2H_2O$) ; rubidium ($Rb_2S_2O_6$) ; ammonium ($(NH_4)_2S_2O_6$) ; argentic ($Ag_2S_2O_6,H_2O$) ; barium ($BaS_2O_6,2H_2O$) ; strontium (SrS_2O_6,H_2O); calcium ($CaS_2O_6,4H_2O$).

Preparation.—By neutralising a solution of the acid with a base, or precipitating a solution of barium dithionate with a soluble sulphate. The dithionate of manganese is prepared by passing SO_2 through ice-cold water containing peroxide of manganese ($MnO_2 + 2SO_2 = MnS_2O_6$).

Properties.—All the dithionates are soluble in water. They crystallise easily. They are decomposed by heat (a sulphate being formed and SO_2 evolved).

The *trithionates* (see page 190) (salts of $H_2S_3O_6$) ; *tetrathionates* (salts of $H_2S_4O_6$), and *pentathionates* (salts of $H_2S_5O_6$) are unimportant.

ACTION OF SULPHURIC ACID ON OXYSULPHO SALTS.

(α.) On *sulphates.* No odor is evolved, either with cold or hot, or with strong or dilute acid.

(β.) On *sulphites.* The odor of SO_2 is evolved with dilute acid in the cold.

(γ.) On *dithionates.* No odor is evolved with dilute acid in the cold, but SO_2 is evolved when the mixture is heated.

(δ.) On *thiosulphates.* The odor of SO_2 is evolved with a dilute acid, the action being accompanied with the deposition of sulphur.

XIV.—Nitrates.

Definition.—Compounds formed from nitric acid (HNO_3). The general formula for the nitrates, nitric acid being monobasic, is $M'NO_3$. No acid nitrates are known, but several sub- or basic nitrates exist ($Cu2NO_3,3CuH_2O_2$).

Synonyms.—*Azotates; Saltpetres.*

Natural History.—Nitrates are produced whenever the ammonia of organic matter is oxidized in the presence of an alkali. They are found in the shallow well-waters of towns as sewage products, formed by the oxidation of the nitrogen during the passage of animal matter through the soil. They are found, too, in the juices of plants, and in the urine of patients who have taken ammonia.

Potassium nitrate (KNO_3) or *prismatic nitre,* is found on the soil in India, the crude nitre, extracted by solution and crystallization, being imported into this country under the name of "grough." *Sodium nitrate* ($NaNO_3$) or *cubical nitre,* is found beneath the soil in Chili and Peru.

Although sodium nitrate is unsuited for gunpowder manufacture, owing to its hygroscopicity and low oxidizing power, it is easily converted into potassium nitrate by the action of potassium chloride, a salt imported into this country from the salt mines of Stassfurth, as well as obtained from the refuse of the beet sugar manufacture ($NaNO_3+KCl=KNO_3+NaCl$).

Nitre heaps or plantations consist of masses of animal refuse mixed with old mortar, etc., and moistened from to time with urine or stable runnings. These heaps are freely exposed to the air, but sheltered from the rain. In time nitrates of the several bases present are formed, and collect both on the surface of the heap and in the superficial layer of earth (nitrified earth). The nitrates are converted into potassium nitrate by potassium carbonate. Thus a cubic metre of earth may be made to yield 20 kilos of nitre.

Theories of Nitrification.—Two theories have been advanced to account for these changes.

I. Schönbein believed that the formation of the nitrates was due to the union of atmospheric oxygen and nitrogen, the combination being favored by the presence of porous solids and of matters undergoing oxidation.

II. Most chemists, however, hold that the nitrogen of the ammonia evolved as the organic matter putrefies, becomes oxidized, the oxidation being promoted by the presence of lime and of porous materials. *Putrefying nitrogenized matters, moisture*, and free access of air are, thereore, the *essential conditions* of nitrification, whilst the presence of a *asic substance*, such as lime, to fix the acid formed, of *porous* materials o assist oxidation, and of an organized ferment (?) (Warrington) are he conditions that specially favor the action.

Impurities of *saltpetres*.—(α.) Insoluble earthy and vegetable matters; β.) potassium and sodium chlorides and sulphates; (γ.) calcium sulhate; (δ.) moisture. Potassium chloride is, moreover, a special mpurity of the potassium nitrate manufactured from sodium nitrate.

Purification of nitre (Refining).—A saturated solution in *boiling* ater of the impure salt is first prepared. This, whilst boiling, is ltered, to remove *insoluble impurities*. The boiling filtrate is then laced in troughs and kept constantly agitated, so that the crystals of otassium nitrate that form may be small (*saltpetre flour*). As the water ools the nitrate crystallizes out, it being four or five times more oluble in hot than in cold water; whilst the sodium and potassium hlorides do not crystallize out, these salts being almost as soluble in old as in hot water. In this way the separation of the chlorides om the nitre is effected. The nitre is then washed with a little ater, the mother-liquor and the washings being afterwards evapoted to dryness, and the residues added to the "grough" or impure tre.

Any coloring matter present is got rid of by animal charcoal. A pure nitre is known—

(1.) By its solution in water being clear and neutral to test-paper.

(2.) By the absence of insoluble matter.

(3.) By argentic nitrate giving no precipitate (proving the absence of chlorides).

(4.) By barium nitrate giving no precipitate (proving the absence of sulphuric acid).

(5.) By ammonium oxalate giving no precipitate (proving the absence of lime).

Preparation (artificial).—By the action of nitric acid on metals, their oxides, or carbonates.

Properties.—The nitrates are all crystallizable solids, of various colors and shapes; some are *rhombohedric* ($NaNO_3$), some *doubly oblique* ($Bi3NO_3$), but most generally *right prismatic.* They have a saline taste, but no odor. Many (K, Na, NH_4, Ba, Pb, Hg) are anhydrous. Some contain four molecules of water (Ca), some five molecules (Sr), whilst the generality contain six molecules of water (Mg, Zn, Ni, Co, Fe, Cu, etc.).

Action of Heat.—They are all decomposed by heat, and generally fuse before decomposing :—

(*α*.) In some cases the metal is entirely reduced by heat (*e.g.*, the nitrates of the noble metals).

(*β*.) In some cases nitric peroxide (N_2O_4) and oxygen are evolved, an oxide remaining ($Pb2NO_3$; $Cu2NO_3$).

(*γ*.) Ammonium nitrate (H_4N,NO_3) breaks up into nitrous oxide (N_2O) and water.

(*δ*.) The alkaline nitrates are first converted into nitrites, oxygen being evolved. By the further application of heat the nitrite is decomposed, with the evolution of nitrogen and oxygen, an oxide remaining.

In the presence of an oxidizable body (such as carbon) the action of heat on the nitrates is very energetic. Thus they deflagrate when placed on red-hot charcoal. (It should be noted that the chlorates and allied salts act similarly.)

Nascent hydrogen decomposes them, forming ammonia.

Sulphuretted hydrogen decomposes the nitrates of those metals that have a strong affinity for sulphuric acid, such as Ba, Pb, etc.

Action of Water.—The nitrates are nearly all soluble in water, except the basic nitrates, such as the green basic cupric nitrate ($Cu2NO_3,3CuH_2O_2$). Mercurous nitrate ($Hg_22NO_3,2H_2O$) and bismuthous nitrate ($Bi3NO_3,5H_2O$) are decomposed by water, a basic salt being formed.

Many of the nitrates are deliquescent, such as $NaNO_3$, $Ca2NO_3$, NH_4NO_3, etc.

Action of Acids.—The nitrates are all decomposed by acids. With *sulphuric acid* nitric acid is set free, and with *hydrochloric acid* chlorine. *The fixed acids* (such as phosphoric, boracic, etc.), decompose the nitrates by heat.

Action of Alcohol.—The nitrates generally are insoluble in alcohol, excepting a few, such as calcium nitrate, cupric nitrate, strontium nitrate, etc.

Tests.—(1.) Hydrochloric acid, mixed with a nitrate, dissolves gold-leaf. (N.B.—A similar result occurs when HCl is added to solutions of chlorates, bromates, and iodates.)

(2.) If a nitrate be heated with a few drops of water, to which a little sulphuric acid and a few copper turnings are added, NO will be evolved, known by its forming red fumes (N_2O_4) in the presence of air or oxygen. (When the nitrate is present in very small quantity, the presence of N_2O_4 may be known by its action on paper moistened with starch and potassium iodide.)

(3.) If a crystal of ferrous sulphate ($FeSO_4$) be dissolved in a nitrate solution, and sulphuric acid be poured down the sides of the test-tube so as to form a layer at the bottom, a brown line will be produced at the junction of the two layers, due to the solution in one portion of the ferrous salt, of the nitric oxide set free by the deoxidizing power of another portion ($6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3(Fe_2 3SO_4) + 2NO + 4H_2O$).

To determine *quantitatively* the nitric acid in saltpetres :—

(1.) Heat for half an hour to dull redness a weighed mixture of the well-dried saltpetre with finely-powdered silica. The nitrate will be decomposed ($2KNO_3 = K_2O + 2NO_2 + O$) and a silicate of potash formed, whilst the sulphates and chlorides present undergo no change. From the mere loss of weight the nitric acid present may be deduced.

(2.) The conversion of the nitrogen of a nitrate into ammonia, by the action of nascent hydrogen (set free either by zinc and sulphuric acid, or by a caustic soda solution and aluminium, or by the action of the copper zinc couple). The ammonia may be estimated by Nesslerising, or by distillation into an excess of hydrochloric acid ($KNO_3 + 4H_2 = NH_3 + KHO + 2H_2O$).

Uses.—For gunpowder, manures, and for the manufacture of nitric acid. The nitrates are in constant requisition in the laboratory as oxidizing agents.

In *medicine,* the ammonic, ferric, plumbic, argentic and potassic nitrates, and a subnitrate of bismuth (really an oxy-nitrate, $BiONO_3$) are officinal.

XV.—Nitrites.

Definition.—Compounds formed from nitrous acid (HNO_2).

History.—Ammonium nitrite has been found in the atmosphere, possibly produced by the combination of atmospheric nitrogen with water as it evaporates ($2H_2O+N_2=NH_4NO_2$), or to the oxidation of ammonia by ozone ($2NH_3+O_3=NH_4NO_2+H_2O$). It is also found in well waters that have been contaminated by organic matter which, containing nitrogen, has undergone partial oxidation. Traces of nitrites have been found in the juices of certain plants.

Preparation.—(1.) By the action of nitrous acid on metallic oxides or hydrates ($KHO+HNO_2=KNO_2+H_2O$).

(2.) By the action of heat on certain nitrates, whereby oxygen is evolved ($Ca2NO_3=Ca2NO_2+O_2$).

(3.) By the oxidation of ammonia or nitrogenized organic matter (as in polluted well-water).

(4.) Nitrites of the alkalies, etc., may be prepared from nitrates, by stirring their boiling solutions with a rod of zinc or cadmium (Schönbein).

(5.) Ammonium nitrite is said to be produced during the spontaneous oxidation of phosphorus in the atmosphere, due to the action of ozone on moist air.

(6.) *Argentic nitrite* may be prepared by the action of potassic nitrite on argentic nitrate.

Properties.—The nitrites are soluble in water and in alcohol, in which latter solvent, for the most part, the nitrates are insoluble. The nitrites of silver, sodium and lead are anhydrous. Several double nitrites have been prepared, as *e.g.*, a compound of nitrite of potassium with a nitrite of either barium, zinc or nickel.

The nitrites (like nitrates, etc.) deflagrate when thrown on glowing carbon.

Acid solutions of the nitrites act both as (α) *oxidizing* agents, as shown by decolorising indigo, and also (β) as *reducing* agents, as shown by their decolorising potassium permanganate, reducing potassium chromate to a green chromium salt, and auric chloride or a mercurous salt to their respective metals.

Tests.—(1.) *Argentic Nitrate.* A white ppt. of argentic nitrite ($AgNO_2$).

(2.) By the action of dilute acids, red fumes are evolved.

(3.) A nitrite solution, acidulated with *a few drops* of sulphuric acid, sets free iodine from KI, which turns blue with starch.

(These tests give no action with nitrates.)

[Note : If organic matter be present in the solution, the nitric acid set free from a nitrate by sulphuric acid, may be reduced, and will then show the reactions of a nitrite. Hence, in such a case, acetic acid should be added, the liquid distilled, and the distillate tested.]

Uses.—Nitrite of ethyl ($C_2H_5NO_2$) is the chief constituent of spiritus ætheris nitrosi (sweet spirit of nitre).

Hyponitrites.

Salts of HNO are of no importance (see p. 130).

SALTS ALLIED TO THE NITRATES.

XVI.—Chlorates (formed from *chloric acid*, $HClO_3$).
XVII.—Bromates (formed from *bromic acid*, $HBrO_3$).
XVIII.—Iodates (formed from *iodic acid*, HIO_3).

We shall consider these together.

Natural History.—None of them are found free in nature.

Preparation.—(1.) By the action of chlorine, bromine, or iodine on a metallic hydrate:—

$$\underset{\text{Potassic hydrate}}{6KHO} + \underset{\text{Chlorine}}{3Cl_2} = \underset{\text{Potassic chloride}}{5KCl} + \underset{\text{Potassic chlorate}}{KClO_3} + \underset{\text{Water.}}{3H_2O.}$$

(Separation may be effected by the greater solubility of the chloride.)

A bromate or iodate is formed when chlorine is passed through a solution of potassic hydrate containing bromine or iodine ($5KHO + Br + 5Cl = KBrO_3 + 5KCl + 3H_2O$).

(2.) By neutralising chloric acid with ammonia or its carbonate ($=NH_4ClO_3$), or by dissolving an oxide in it ($HgClO_3$).

(3.) *Ammonium Chlorate* (NH_4ClO_3). By acting on ammonium fluosilicate with potassium chlorate, and evaporating the clear solution over sulphuric acid.

(4.) *Mercurous Bromate* ($HgBrO_3$). By mixing together solutions of mercurous nitrate and potassic bromate.

Properties.—The chlorates, bromates, and iodates are all very nearly related to the nitrates. In one respect the *iodates* are peculiar, viz., that a basic molecule may combine with more than one molecule of the acid; in other words, that iodic acid, though a monobasic acid, forms hyper-acid salts. Thus we have—

(1.) *Normal potassic iodate* (KIO_3); (2.) *Acid potassic iodate* (KIO_3, HIO_3); (3.) *Di-acid potassic iodate* ($KIO_3,2HIO_3$).

Action of Heat.—The chlorates, bromates, and iodates are all decomposed by heat, often with explosion, one of two results occurring:—

(*a.*) Oxygen only may be driven off—a *chloride, bromide*, or *iodide* remaining. This occurs if the affinity of the metal for the haloid is greater than it is for oxygen. Thus $2KIO_3 = 2KI + 3O_2$; or conversely—

(β.) Oxygen and the haloid element may both be given off, an *oxide* remaining. This occurs if the affinity of the metal for oxygen is greater than it is for the haloid. Thus $2(Ba2IO_3) = 2BaO + 5O_2 + 2I_2$.

Mixed with a combustible element they all deflagrate when heated and explode when struck. Paper soaked in their solutions and dried burns like touch-paper. Ammonium bromate often explodes spontaneously.

Action of Acids.—They are all decomposed by acids. *Sulphuric acid* sets free from the chlorates the yellow chlorine compounds, whilst from the bromates and iodates, oxygen and bromine, or oxygen and iodine, are set free respectively. *Hydrochloric acid* also liberates chlorine compounds from the chlorates, and chlorine with bromine, or chlorine with iodine, from the bromates and iodates respectively. *Nitric acid* forms with the chlorates a nitrate and a perchlorate, with the liberation of oxygen and chlorine.

Action of Water.—The *chlorates* are nearly all soluble in water, and are deliquescent (mercurous chlorate excepted). The ammonium chlorate, when boiled in water, evolves nitrogen and chlorine. The *bromates* are mostly soluble, although with difficulty, in water, the mercurous, silver and lead bromates being the least soluble. The *iodates*, excepting the alkaline iodates, are but sparingly soluble in water.

Action of Alcohol.—Many of the salts are soluble in alcohol.

All the salts of this group act as oxidizing agents. The chlorates for this purpose are in constant use in the laboratory, chloric acid being set free by the action of hydrochloric acid upon them. Making use of this reaction, most protosalts may be changed to persalts.

Tests.—They all deflagrate when placed on red hot charcoal.

Chlorates.—(1.) No precipitate with *argentic nitrate.* [A chlorate is by this reaction known from a chloride.] If the salt be one (like $KClO_3$) forming a chloride by heat, the solution of the residue after ignition (KCl) will give a precipitate of $AgCl$ with argentic nitrate.

(2.) Add a few drops of indigo to a solution of a chlorate. On the addition of a solution of sulphurous acid, the indigo will be bleached. A chlorate may in this way be known from a nitrate, for with the latter the blue color remains unaltered.

(3.) On heating a chlorate with HCl, yellowish green vapors are evolved (*euchlorine*).

(4.) On adding sulphuric acid to a chlorate, *chloric peroxide* (ClO_2) is evolved (p. 99).

Bromates.—Bromine is set free when a bromide is heated with sulphuric acid.

Iodates.—If a sulphurous acid solution be added to a solution of an iodate, an iodide is formed ($KIO_3+3H_2SO_3=KI+3H_2SO_4$). The iodide may then be detected in the usual way, with $AgNO_3$ or by starch.

OTHER OXY-SALTS OF CHLORINE, BROMINE, AND IODINE.

XIX.—Perchlorates.

Salts formed from *perchloric acid* ($HClO_4$). *Examples*—$NaClO_4$; $LiClO_4$; $RbClO_4$; NH_4ClO_4; $Ba2(ClO_4),4H_2O$.

Preparation.—Potassium perchlorate may be formed either by heating potassium chlorate, but discontinuing the heat so soon as one-third of the oxygen has been evolved ($2KClO_3 = KCl + KClO_4 + O_2$); or by acting on potassic chlorate with boiling nitric acid ($3KClO_3 + 2HNO_3 = 2KNO_3 + H_2O + KClO_4 + Cl_2 + 2O_2$).

Mercurous perchlorate ($HgClO_4$) may be formed by the action of perchloric acid on mercurous oxide.

Properties.—The *perchlorates* are all soluble in water, and many are soluble in alcohol. They are all decomposed by heat, with the formation of a chloride and the evolution of oxygen. They are not decomposed by hydrochloric acid. Heated with strong sulphuric acid they do not yield chloric peroxide.

To distinguish a perchlorate from a chlorate:—(1.) Add a few drops of sulphuric acid to some crystals of the salt. A yellow gas will be evolved in the case of chlorates, but none in the case of perchlorates.

(2.) The perchlorates are not acted upon by hydrochloric acid like chlorates.

(3.) They require a higher temperature for their decomposition than chlorates.

XX.—Periodates.

Salts formed from *periodic acid* (HIO_4). *Examples*—KIO_4; $NaIO_4, 3H_2O$; $AgIO_4$.

The *periodates* are of four kinds: mono-, tri-, 'tetra-, and penta-basic respectively, and may be represented as salts of acids formed of I_2O_7, with 1, 2, 3, or 5 molecules of water. The salts (which are very complex), are sparingly soluble in water, but soluble in dilute nitric acid. They are all decomposed by heat. Their solutions, slightly acidulated with HNO_3, give a dark brown precipitate of (Ag_5IO_6) (para-periodate) with argentic nitrate, soluble in excess of nitric acid, the solution on evaporation yielding yellow crystals of $AgIO_4$ (meta-periodate), which, when added to water, splits up into the free acid and $Ag_4I_2O_9$ (di-periodate). Periodic acid has a tendency to form *basic* salts, just as iodic acid has a tendency to form *acid* salts.

Sodium periodate may be formed by the action of chlorine on a mixed solution of sodic hydrate and iodate ($NaIO_2 + 2NaHO + Cl_2 = NaIO_4 + H_2O + 2NaCl$).

XXI.—Chlorites.

Definition.—Salts formed from chlorous acid ($HClO_2$).

Preparation.—By the action of chlorous acid upon a base. The yellow crystalline lead and silver chlorites may be prepared by adding lead or silver nitrate to a soluble chlorite.

Properties.—The chlorites are solid deliquescent salts, decomposed by heat and by the feeblest acids (as CO_2). They possess considerable bleaching power, and deoxidize an acidulated solution of potassium permanganate.

XXII.—Hypochlorites.

Definition.—Salts formed from hypochlorous acid ($HClO$) (p. 97).

Preparation.—By the action of hypochlorous acid on metallic oxides or hydrates :—

$$\underset{\text{Potassic hydrate}}{KHO} + \underset{\text{Hypochlorous acid}}{HClO} = \underset{\text{Potassic hypochlorate}}{KClO} + \underset{\text{Water.}}{H_2O.}$$

Properties.—The hypochlorites are bleaching salts, and are decomposed by the feeblest acids. Heat decomposes them, a chloride and a chlorate resulting ($3KClO = 2KCl + KClO_3$).

The interest of the hypochlorites is centred in what is called "*chloride of lime*," or bleaching powder. This is prepared by acting with chlorine on slaked lime (calcic hydrate). The temperature has to be maintained below 100° F., or otherwise calcium chloride and chlorate would be formed. The potassium and sodium chlorides are prepared in a similar manner. It was formerly thought that a *chloride* and a *hypochlorite* were formed during this process. Thus—

$$\underset{\text{Calcium hydrate}}{2CaH_2O_2} + \underset{\text{Chlorine}}{2Cl_2} = \underset{\text{Calcium chloride}}{CaCl_2} + \underset{\text{Calcium hypochlorite}}{Ca''Cl_2O_2} + \underset{\text{Water.}}{2H_2O.}$$

but of this there is considerable doubt, inasmuch as bleaching-powder contains no calcium chloride, and is not deliquescent when properly made. Hence the composition of bleaching-powder is usually stated as consisting of a calcium chloride hypochlorite, $CaCl(OCl)$. Thus—

$$\underset{\text{Calcic hydrate}}{CaH_2O_2} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Bleaching powder}}{CaCl(OCl)} + \underset{\text{Water.}}{H_2O.}$$

When "*chloride of lime*" is exposed to the air it gives off chlorine, by the action upon it of atmospheric carbonic anhydride. Hence its use as a disinfectant. The evolution of chlorine is considerable when a strong acid is added to the compound ($Ca(OCl)Cl + H_2SO_4 = CaSO_4 + H_2O + Cl_2$). It is also used as a bleaching agent (chlorine exerting a powerful oxidizing action), the goods being first digested in a solution of bleaching powder, and afterwards transferred to a weak acid solution, whereby the chlorine is set free.

To distinguish a hypochlorite from a chlorite, add to the solution of the salt a solution of arsenious anhydride and nitric acid ; the bleaching power of the *chlorites* remains unaffected, whilst that of the *hypochlorites* is destroyed.

XXIII.—Phosphates (page 161).

(α.) *Orthophosphates*, compounds formed from orthophosphoric acid, H_3PO_4.
(β.) *Pyrophosphates*, „ „ pyrophosphoric acid, $H_4P_2O_7$.
(γ.) *Metaphosphates*, „ „ metaphosphoric acid, HPO_3.

(α.)—ORTHOPHOSPHATES, or *Common Phosphates.*

Definition.—Salts of tribasic phosphoric acid, H_3PO_4.

Varieties of Orthophosphates.—One or all of the hydrogens of the acid may be replaced by a metal. Thus :—

NaH_2PO_4 = Sodium-dihydrogen phosphate (superphosphate) } *Acid salts.*
Na_2HPO_4 = Disodium-hydrogen phosphate }
Na_3PO_4 = Trisodium phosphate ... *Normal salt.*

Or the three hydrogens may be replaced by different metals. Thus—$HNaNH_4PO_4 + 4aq$ = Hydric sodium ammonium phosphate (*microcosmic salt*).

Preparation.—KH_2PO_4 is prepared by mixing together solutions of potassium carbonate and phosphoric acid, so that the solution is strongly acid.

K_2HPO_4 is prepared by mixing together solutions of potassium carbonate and phosphoric acid to slight alkalinity.

K_3PO_4 is prepared by igniting two molecules of phosphoric anhydride with three of potassium carbonate.

Properties.—The orthophosphates are solid salts, having a saline taste but no odor. They fuse by heat, but they are not decomposed if the base of the salt be a fixed one. Acids (even carbonic) decompose and dissolve them. The phosphates of the alkalies are soluble in water, the remainder being insoluble. The insoluble phosphates, excepting calcium phosphate, are decomposed on boiling with sodium carbonate.

Tests.—(1.) *Argentic nitrate;* a yellow ppt. (Ag_3PO_4) in a neutral solution ($NaH_2PO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + 2HNO_3$).

(2.) *Magnesium sulphate and ammonia;* a white ppt. ($NH_4MgPO_4 + 6H_2O$), which by heat becomes $Mg_2P_2O_7$ (100 parts = 63·96 of P_2O_5).

(3.) *Ammonium molybdate;* a yellow ppt. when boiled in a solution containing HNO_3.

(β.) PYROPHOSPHATES.

Definition.—Salts of pyrophosphoric acid ($H_4P_2O_7$), a tetrabasic acid.

Preparation.—By heating tribasic phosphates. Thus, *sodium* *pyrophosphate* is prepared by igniting common sodium phosphate ($2Na_2HPO_4 = H_2O + Na_4P_2O_7$).

Most of the pyrophosphates are solid. They are easily converted into meta- and ortho-phosphates, by the addition or abstraction of water, or of a metallic base. The alkaline pyrophosphates are soluble in water, and slake when boiled. By boiling with dilute acids, they become tribasic phosphates. They usually dissolve in an alkaline pyrophosphate, forming a double salt.

Tests.—*Argentic nitrate ;* a white ppt. in alkaline solutions ($Ag_4P_2O_7$).

(γ.) METAPHOSPHATES.

Definition.—Salts of metaphosphoric acid (HPO_3).

Preparation.—The metaphosphates are generally prepared by igniting a superphosphate of a fixed base ($NaH_2PO_4 = NaPO_3 + H_2O$). *Sodium metaphosphate* is prepared by the ignition of dihydric sodium phosphate or of microcosmic salt ($HNaNH_4PO_4 = NaPO_3 + NH_3 + H_2O$).

Properties.—The soluble metaphosphates are converted into dihydric tribasic phosphates by boiling with water, the insoluble salts undergoing similar conversion by boiling in dilute nitric acid.

Test.—*Argentic nitrate ;* a white gelatinous ppt. ($AgPO_3$).

Other phosphates have been studied by Fleitmann and Henneberg. They are formed by fusing together (α) one part of pyrophosphate and two of metaphosphate, the salt formed having the composition $2Na_3PO_4,P_2O_5$; and (β) one part of pyrophosphate and eight of metaphosphate, the salt formed having the composition $4Na_3PO_4, 3P_2O_5$. They are unstable salts, but form definite argentic and magnesic compounds (*see* page 166).

All phosphates are converted into tribasic phosphates by fusion with an alkaline hydrate or carbonate.

OTHER OXY-PHOSPHORUS SALTS.

XXIV.—Hypophosphites.

Definition.—Salts formed from hypophosphorous acid (H_3PO_2 or HH_2PO_2) (p. 159). The acid is monobasic.

Preparation.—By acting on a metallic hydrate with phosphorus ($P_8 + 6H_2O + 3CaH_2O_2 = 3(Ca''2H_2PO_2) + 2PH_3$.

Properties.—The salts are monobasic, as, *e.g.*, NaH_2PO_2, or $CaH_4P_2O_4$, and $Pb''2H_2PO_2$. They are all deliquescent, crystalline, stable solids. By evaporating down their solutions, they are converted into phosphites. The hypophosphites reduce gold and silver salts. They are all soluble in water, the alkaline hypophosphites being also soluble in alcohol. They are all decomposed by heat.

"*Sodæ hypophosphis*" is a pharmacopœial preparation.

XXV.—Phosphites.

Definition. — Salts formed from phosphorous acid (H_3PO_3). (p. 160).

Phosphorous acid in certain compounds plays the part of a tribasic acid (*e.g.* $(C_2H_5)_3PO_3$). As regards the metals it is dibasic (page 161).

Phosphites may be *normal* (M'_2HPO_3), or *acid* ($M'HHPO_3$).

Preparation.—By neutralising the aqueous acid with an alkaline hydrate or carbonate.

Properties.—Solid bodies, sparingly soluble in water, except the phosphites of the alkalies, which are freely soluble. The soluble phosphites act as reducing agents. On the application of heat, the *normal* phosphites evolve hydrogen and phosphoretted hydrogen, whilst the *acid* phosphites evolve hydrogen only leaving a metaphosphate.

Tests.—(1.) *Mercuric chloride ;* a white ppt. of calomel in a solution acidulated with acetic acid.

(2.) *Sulphurous acid* is reduced by the phosphites to H_2S, a precipitation of sulphur resulting from the action of the H_2S on the excess of sulphurous acid ($3H_3PO_3 + H_2SO_3 = 3H_3PO_4 + H_2S$).

ALLIES OF THE PHOSPHATES.

Arsenates (salts of arsenic acid, H_3AsO_4) ; *Antimonates* (salts of antimonic acid, or antimonic anhydride, Sb_2O_5) ; *Vanadates* (salts of vanadic acid or vanadic anhydride, V_2O_5).

XXVI.—Arsenates.

Definition.—Salts formed from arsenic acid (H_3AsO_4).

The arsenates are allied to and isomorphous with the phosphates. Thus—

$Na_3AsO_4,12H_2O$ is prepared by adding an excess of sodic hydrate to arsenic acid, and evaporating.

$Na_2HAsO_4,12H_2O$ is prepared by adding sodium carbonate to a hot solution of arsenic acid until effervescence ceases, and evaporating.

NaH_2AsO_4,H_2O is prepared by adding to the previous salt an equivalent quantity of arsenic acid to that which it already contains.

KH_2AsO_4 is prepared by fusing together nitre and arsenious acid, dissolving the residue in water, and crystallizing.

$(H_4N)MgAsO_46H_2O$ (a body isomorphous with the phosphate salt), is prepared by adding magnesium sulphate to a solution of an alkaline arsenate to which ammonia has been added.

EXAMPLES.

Potassium arsenates	K_3AsO_4. K_2HAsO_4. KH_2AsO_4.
Sodium arsenates	$Na_3AsO_412H_2O$. $Na_2HAsO_412H_2O$. $Na_4As_2O_7$ (Pye). $NaH_2AsO_4H_2O$.
Argentic arsenates	Ag_3AsO_4.
Magnesium arsenates	$Mg_32(AsO_4)$. $MgHAsO_47H_2O$. $MgNH_4AsO_47H_2O$.
Cupric arsenate	$Cu_3AsO_82H_2O$.

Properties.—In form and reactions the arsenates are very similar to the tribasic phosphates. Arsenates corresponding to the meta- and pyro-phosphates ($Na_4As_2O_7$) are also known. Anhydrous arsenates may be prepared. Heat alone, provided a fixed base be present, does not decompose them. They are decomposed by nascent hydrogen, arseniuretted hydrogen being evolved. Acids decompose them. Water dissolves the alkaline arsenates only, but all the arsenates are soluble in dilute nitric acid.

Tests.—(1.) *Lime, lead,* and *barium salts;* white ppts.

(2.) *Argentic nitrate;* a brownish-red ppt. of triargentic arsenate (Ag_3AsO_4). (This test distinguishes the arsen*ates* from the arsen*ites.*)

(3.) *Sulphuretted hydrogen;* a yellow ppt. of As_2S_5, soluble in ammonia.

(4.) Add a few drops of *cupric sulphate,* and carefully drop in *dilute ammonia* until a green precipitate is produced ($CuHAsO_4$). *The arsenate solution must be neutral.* The cupric arsenate is soluble in acids and in alkalies.

Uses.—The arsenate of soda and the arsenate of iron (Fe_32AsO_4) are used in *medicine.*

XXVII.—Vanadates.

Salts of vanadic acid, or more correctly, compounds of a base and vanadic anhydride (V_2O_5) (Roscoe). Vanadic acid is only known in its salts, of which ortho-, meta- and pyro-vanadates, isomorphous with phosphates, have been prepared. In addition to these, certain tetravanadates are known.

Orthovanadates, compounds of orthovanadic acid H_3VO_4.
Metavanadates, „ „ metavanadic acid HVO_3.
Pyrovanadates, „ „ pyrovanadic acid $H_4V_2O_7$.

The vanadates are usually red or yellow bodies. Boiled with sulphuric acid, alcohol, and sugar, or heated with sulphuretted hydrogen or sulphurous acid, they form a deep blue solution.

XXVIII.—Antimonates.

Salts of antimonic acid ($HSbO_3$). These closely resemble the arsenates. The alkaline salts are obtained by the action of antimonic anhydride (Sb_2O_5) on a hydrate, or by deflagrating antimony and a nitrate. They are decomposed by an acid, $Sb_2O_5,4H_2O$ being precipitated. There are said to be two modifications of antimonic acid, viz., *antimonic acid* ($HSbO_3$ or Sb_2O_5,H_2O), forming normal salts, such as $KSbO_3$, and *metantimonic acid* ($H_4Sb_2O_7$ or $Sb_2O_5,2H_2O$), which also forms a normal salt, such as $K_4Sb_2O_7$.

The *soluble acid metantimonate of potassium* ($K_2H_2Sb_2O_7,6H_2O$) precipitates soda-salts as an insoluble acid sodium metantimonate ($Na_2H_2Sb_2O_7,6H_2O$). The acid potassic salt rapidly changes to a normal salt, but this latter does not effect the precipitation of sodium compounds.

XXIX.—Sulph-Arsenates (Salts of H_3AsS_4).

Examples of these are found in K_3AsS_4 and $(Na_3AsS_4)_2 15H_2O$.

Preparation.—(1.) By passing sulphuretted hydrogen through solutions of arsenates :—

Na_2HAsO_4	+	$4H_2S$	=	Na_2HAsS_4	+	H_2O.
Sodium arsenate		Sulphuretted hydrogen		Sodium sulpharsenate.		Water.

(2.) By dissolving arsenic sulphide and sulphur in a solution of an alkaline sulphide or sulphhydrate :—

$$As_2S_3 + 3K_2S + S_2 = 2K_3AsS_4.$$

Properties.—With dilute acids (cold) the sulpharsenates yield H_3AsS_4, which on boiling yields As_2S_5 and H_2S ($H_3AsS_4 = As_2S_5 + 3H_2S$).

XXX.—Sulph-Antimonates (Salts of H_3SbS_4).

Examples—K_3SbS_4; (Schleppe's Salt, $Na_3SbS_4,9H_2O$).

The preparation and properties of these compounds resemble the sulph-arsenates.

XXXI.—The Arsenites.

Salts of H_3AsO_3 or $As_2O_3,3H_2O$.

The arsenites of the alkalies may be formed by dissolving arsenious anhydride (As_2O_3) in solutions either of the alkalies or of the alkaline carbonates. M'_3AsO_3 (orth-arsenites) and $M'AsO_2$ (met-arsenites) are formulæ.

Examples.—Ag_3AsO_3 and $CuHAsO_3$ are the formulæ believed to represent the composition of these salts. The alkaline arsenites are soluble in water. The arsenites of the earths are insoluble in water but are soluble in acids.

Potassium arsenite (Fowler's solution, or liquor arsenicalis) (KH_2AsO_3), is used in medicine. The alkaline arsenites are used as sheep-dipping mixtures, and also by naturalists as an arsenical soap to preserve the skins of animals. Sodium arsenite is used to prevent the incrustation in boilers.

Cupric arsenite, or "*Scheele's green*," ($CuHAsO_3$), and a mixed *cupric arsenite and acetate*, or "*Schweinfurt green*" ($3CuAs_2O_4,Cu2C_2H_3O_2$) and argentic arsenite (Ag_3AsO_3) are used as pigments.

The arsenites are unstable compounds, having a great tendency to become arsenates by the absorption of oxygen. They are decomposed by CO_2.

Antimonites.—Sodium metantimonite ($NaSbO_2,3H_2O$) is formed by adding antimonious anhydride to a solution of caustic soda.

XXXII.—Sulph-Arsenites (Salts of H_3AsS_3).

Example—Ag_3AsS_3 (argentic sulpharsenite).

By dissolving arsenious sulphide in an alkaline sulphide :—

$$\begin{array}{ccccc} As_2S_3 & + & 3K_2S & = & 2K_3AsS_3. \\ \text{Arsenious sulphide} & + & \text{Potassium sulphide} & = & \text{Potassium sulpharsenite.} \end{array}$$

XXXIII.—Sulph-Antimonites (Salts of H_3SbS_3).

Example—Ag_3SbS_3 (dark red silver ore).

Of the sulph-antimonites may be noted :—

Ortho-sulph-antimonites	...	M'_3SbS_3 or $M''_3Sb_2S_6$.
Meta ,,	...	$M'SbS_2$ or $M''Sb_2S_4$.
Pyro ,,	...	M'_4SbS_5 or $M''_2Sb_2S_3$.

Preparation of ortho compounds. By the action of sulph-hydrate on antimonious sulphide:—

$$\begin{array}{ccccc} Sb_2S_3 + 6KHS & = & 2K_3SbS_3 & + & 3H_2S. \\ & & \text{Potassic sulph-} & & \\ & & \text{antimonite.} & & \end{array}$$

XXXIV.—Carbonates.

Definition.—Salts formed from carbonic acid (H_2CO_3). Although this acid is not known in a free state, it no doubt exists in solution when CO_2 is dissolved in water. The acid is dibasic, forming both acid and normal salts, the acid carbonates of the alkalies being the only solid acid carbonates known.

Natural History.—The carbonates are found in all three kingdoms of nature ; (α) in the *mineral* kingdom (as *e. g.*, $CaCO_3$, etc.); (β) in the *vegetable*, as, *e. g.*, pearlash (K_2CO_3) in the ashes of land-plants, and sodium carbonate in the ashes of marine plants; (γ) in the *animal* kingdom, carbonates are found in bones, shells, blood, urine deposits, etc.

Preparation.—(1.) Sodium carbonate is prepared from sodium chloride, by first converting it into a sulphate, and afterwards heating it with chalk and coal (*see* Sodium Carbonate).

(2.) From the ashes of plants by lixiviating.

(3.) By the action of an alkaline carbonate on a metallic salt ($Pb_2NO_3+Na_2CO_3=2NaNO_3+PbCO_3$).

[N.B.—The carbonates are never formed by the action of carbonic anhydride on a dry metallic oxide.]

Properties.—The carbonates are very stable bodies. They generally crystallize in right prisms; some in oblique prisms (Na), and some in rhomboids (Ca, Fe, Zn).

Action of Heat.—Ammonium carbonate volatilizes when heated. The carbonates of the alkaline metals and of barium are unaffected by a white heat. All other carbonates are decomposed at a high temperature, CO_2 being evolved, and a metallic oxide left.

Action of Acids.—All carbonates are decomposed by acids, with the evolution of CO_2.

Action of Water.—The alkaline carbonates are soluble in water. Many carbonates that are insoluble in common water, are soluble in water containing CO_2 in solution, but are deposited as soon as the CO_2 escapes. Many of them are anhydrous.

Tests.—An acid sets free CO_2 which whitens baryta or lime-water (forming $BaCO_3$ and $CaCO_3$), the precipitates being soluble in an acid.

Uses.—The sodium salt is largely used in every-day life, and also in medicine. The ammonium, bismuth (really an oxycarbonate), ferrous (which mixed with sugar forms the saccharated carbonate), lithium, magnesium, potassium, and zinc carbonates are also used medicinally.

Certain *sulpho-carbonates* have been prepared, of which potassium sulpho-carbonate (K_2CS_3) is an example.

XXXV.—Silicates.

Definition.—Compounds of H_4SiO_4 (*tetrabasic silicic acid*), and also of H_2SiO_3 (*dibasic silicic acid*), this latter acid being said to be produced by the evaporation "in vacuo" of a solution of the tetrabasic acid.

Natural History.—Silicates are found in nature abundantly, as peridote, eustatite, ophite, talc, serpentine, steatite, meerschaum (magnesic silicates), okenite (calcic silicate), diopside (calcic magnesic silicate), pyrophyllite (aluminic silicate), anorthite, labradorite, grossularia (aluminic calcic silicates). Phenacite (beryllic silicate), emerald (beryllic aluminic silicate), felspar (potassic aluminic silicate), chloropal (iron silicate), zircon (zirconic silicate), willemite (zincic silicate), etc.

Varieties.—The salts having the formula M'_4SiO_4, have been named *ortho-silicates*, and the salts with the formula M'_2SiO_3 *meta-silicates*. There exists also an intermediate class, formed by the combination of a molecule of each. The double silicates are numberless.

Preparation of Alkaline Silicates.—By fusing silicic anhydride or the insoluble silicates, with the alkaline hydrates or carbonates.

Properties.—*Action of Heat.*—The silicates are mostly fusible, their fusibility being increased by admixture.

Action of Water.—They are all insoluble in water, excepting the alkaline silicates containing an excess of base.

Action of Acids.—The anhydrous, normal and acid silicates of the earths, are not decomposed by any acid except hydrofluoric. The hydrated silicates are decomposed by all acids. If CO_2 be passed through a solution of sodium silicate, silicic acid is precipitated as a gelatinous deposit.

The silicates are alkaline to turmeric.

The **Silico-fluorides** or **Fluo-silicates** are salts of hydrofluosilicic acid (H_2SiF_6). Treated with an excess of base they undergo decomposition, forming silicates and fluorides ($K_2SiF_6 + 8KHO = K_4SiO_4 + 6KF + 4H_2O$). The silico-fluorides of potassium and barium are insoluble in water.

XXXVI.—Borates.

Salts of boric acid, H_3BO_3, are formed by the action of the acid on metallic hydrates, oxides or carbonates.

The following are examples :—

Potassium borates	KBO_2 (*meta*). $KHB_2O_42H_2O$. $K_2B_4O_7, 6H_2O$ (*pyro*). $KHB_6O_{10}, 4H_2O$.
Rubidium borate	$Rb_2B_4O_7,6H_2O$.
Ammonium borates	$(NH_4)_2B_4O_7$. $NH_4, HB_4O_73H_2O$.
Magnesium borate	$Mg_32B_2O_3$ (*ortho*).

The metaborate of potassium (KBO_2), is prepared by fusing boric anhydride with potassium carbonate. A potassium hydric borate ($KH,2(BO_2)2H_2O$) ; also $K_2B_4O_7,6H_2O$; also $KHB_6O_{10},4H_2O$ are some of the other borates of potassium that have been prepared.

The borates resemble the silicates in the variety of the proportions in which they enter into combination with the alkaline bases. All the borates are more or less soluble in water, the alkaline borates being very soluble, and the others less so. They are all soluble in dilute nitric acid. The borates impart a green light to flame.

XXXVII.—Double Salts.

Definition.—Salts in which the displaceable hydrogens of the acid have been exchanged by different metals or compound radicals.

Varieties.—(I.) *Salts formed by a combination of two metals with the same acid radical*:—

(*a.*) The bicarbonates ($HNaCO_3$), binoxalates, etc., are thus double salts, the hydrogen playing the part of a metal.

(*β.*) One hydrogen of a dibasic acid may be displaced by one metal, and the second hydrogen by a different metal, as in Rochelle salt where sodium and potassium are combined with tartaric acid ($KNaC_4H_4O_6$), or as in the sodium potassium disulphate (NaK_32SO_4), where $2SO_4$ is combined with K_3 and Na.

Thus we have double sulphates, double carbonates, double silicates, etc.

(II.) *Combinations of oxides of different classes with their several equivalents of the acid radical*:—

Thus in common alum we have a sulphate of potash combined with a sulphate of alumina ($K_2O,SO_3+Al_2O_33SO_3$), forming the compound $K_2Al_24SO_4+24aq$.

(III.) *Combinations of salts with saline or constitutional water*:—

Thus one molecule of water in magnesic sulphate ($MgSO_4,H_2O+6H_2O$) cannot be expelled by a heat of 212° F., as the other six molecules of water may be. This seventh molecule of H_2O, may be regarded as a salt (hence called saline water), and may be replaced by a molecule of certain anhydrous salts not isomorphous with it, such as potassium sulphate, forming ($MgSO_4,K_2SO_4,6H_2O$).

(IV.) *The combination of two acid radicals with one basic radical.* These are comparatively unimportant, and can scarcely be regarded as true double salts.

(V.) *The combination of haloid salts with haloid salts*, such as potassium chloride with platinic chloride ($2KCl,PtCl_4$).

Preparation.—Double salts are prepared (1) either by the admixture of solutions of two salts in equivalent proportions, or (2) by the fusion of the two salts.

The following are some of the double salts:—

1. **Double Haloid Salts.**—*Where an alkaline haloid salt is combined with a haloid salt of a metal having a feebler affinity for oxygen than the alkaline salt*, as *e.g.* ($2KCl,PtCl_4$); ($NaCl,AuCl_3,2H_2O$).

2. **Double Sulphur Salts.**—(*a.*) *Double sulphides*, as *e.g.*, alkaline sulphides with higher sulphides ($3Na_2S,As_2S_5,15H_2O$); ($3Na_2S,Sb_2S_5,18H_2O$). (*β.*) *Hydrosulphides*, as *e.g.*, (KHS); (MgH_2S_2). (In these salts H acts as a metal.)

3. **Double Oxysalts.**—(*a.*) *Double sulphates*, such as the *acid sulphates* or *bisulphates* ($NaHSO_4$); the *alums*; and such other double

sulphates as Na_2Ca2SO_4 (*glauberite*), $MgSO_4,K_2SO_4,6H_2O$; and also soda with magnesia, potash with manganese or with zinc, etc.

(β.) *Double carbonates*, such as $MgCa2CO_3$ (*dolomite*), $BaCa2CO_3$ (*baryto-calcite*), etc.

(γ.) *Double silicates*, such as silicate of alumina with silicate of potash (*felspar*), or with silicate of soda (*albite*), or with silicate of lime (*anorthite*), or with silicate of glucinum (*emerald*), etc. *Porcelain* is a double silicate of lime and alumina; *glass*, of potash or of soda with silicate of lime, magnesia, alumina, lead, etc.

(δ.) *Double tartrates*, such as Rochelle salt. Similarly there are *double citrates*, etc.

CHAPTER XIII.

THE ALKALINE METALS.

	Symbol.	Atomic Weight.	Specific Heat.	Fusing Point.		Specific Gravity.	Electric Conductivity. 68–71F.
				°C.	°F.		
Potassium	K	39·0	0·16956	62·5	144·5	0·865	20·85
Sodium	Na	23·0	0·29340	97·6	207·7	0·972	37·43
Lithium	Li	7·0	0·94080	180·0	356·0	0·593	19·0
Cæsium	Cs	133·0	(?)	26·5	77·8	1·88	—
Rubidium	Rb	85·3	0·077	38·5	101·3	1·52	—
Ammonium	NH_4 (or Am)	18·0					—

General Remarks.

Characters.—The alkaline metals decompose water at ordinary temperatures. They form soluble oxides, sulphides, hydric sulphides, and carbonates. The carbonates have an alkaline reaction.

History.—The existence of the alkaline metals was prophesied by Lavoisier (1793). Sir H. Davy obtained potassium and sodium n 1807, by decomposing the alkalies with the galvanic battery. Lithia was first prepared by Arfvedson in 1817, the existence of the metal lithium being afterwards demonstrated by Davy. It was first prepared in quantity by Matthiessen (1855). ("Phar. Journ.," XV., p. 231.) Rubidium and cæsium were discovered by Bunsen and Kirchhoff in 1860 by their peculiar spectra.

General Properties.—(α.) *Physical.* The alkaline metals are soft, easily fusible, and volatile.

(β.) *Chemical.* They tarnish rapidly in the air. They decompose water, liberating hydrogen at ordinary temperatures. They are univalent. They furnish several oxides, but only one basic oxide (M'_2O), which is very deliquescent, very caustic, and very alkaline o test paper. The hydrates (MHO) cannot be decomposed by heat. They rapidly absorb CO_2, forming both normal and acid carbonates. The alkaline metals form but one chloride. Nearly all their salts are oluble and alkaline.

POTASSIUM (K_2).

Atomic weight, 39·0. *Atomicity, monad* (′) (KCl, KI). *Specific gravity*, 0·865. *Fuses at* 144·5° F. (62·5° C.). *Boils at a low red heat.*

History.—Isolated by Davy (1807). [K = Kalium.]

Natural History.—Found (*a.*) in the animal kingdom; (*β.*) in the vegetable kingdom, as a sulphate and chloride, and combined with vegetable acids ; (*γ*) in the mineral kingdom in various combinations, such as *potash felspar* or *orthoclase* ($K_2Al_2Si_6O_{16}$) ; *leucite* ($K_2Al_2Si_4O_{12}$) ; *carnallite* ($KCl, MgCl_2, 6H_2O$), etc.; also in sea and spring water, etc.

Preparation.—(1.) (*Ordinary process.*) By decomposing potassium carbonate with charcoal (Curandau and Brunner). Thus :—

(*a.*) The crude tartar from wine casks ($KHC_4H_4O_6$) is incinerated, a mixture of potassium carbonate with carbon being formed :—

$2KHC_4H_4O_6$	=	K_2CO_3	+	$5H_2O$	+	$4CO$	+	$3C.$
Hydric potassium tartrate.	=	Potassium carbonate	+	Water	+	Carbonic oxide	+	Carbon.

(*β.*) The residue is now intensely heated in an iron retort, the potassium being distilled into a receiver containing naphtha—

K_2CO_3	+	C_2	=	$3CO$	+	$K_2.$
Potassium carbonate	+	Carbon	=	Carbonic oxide	+	Potassium.

(Chalk is commonly added to the mixture to prevent fusion.)

The metal is redistilled to get rid of absorbed CO, otherwise the potassium is liable to explode.

(2.) By the electrolysis of potassium hydrate (Davy, 1807), the metal and hydrogen being evolved at the negative pole.

(3.) By the action of white hot iron on potassium hydrate (Gay Lussac, 1808), ($4KHO+3Fe=Fe_3O_4+2K_2+2H_2$).

Properties.—(*a.*) *Physical.* Potassium is a soft and silvery-white metal. It may be obtained in crystals by fusion in an atmosphere of coal gas, and pouring off the liquid portion. The specific gravity of the metal (0·865), being less than water, it floats upon it. It is brittle and crystalline at 32° F. (0° C.), but becomes malleable a little above this temperature. It fuses at 144·5° F. (62·5° C.), and boils at a low red heat, when it evolves a green gas. Its spectrum consists of two lines at A and B, and a third violet line in the blue end.

(*β.*) *Chemical.* It has a strong affinity for oxygen, oxidizing instantly in air ; hence it is commonly preserved under naphtha. It burns with a violet flame when heated. When brought up to a red heat in an atmosphere of CO_2 or of CO, it liberates carbon ($CO_2+2K_2=2K_2O+C$), the carbon at a higher temperature reducing the potassium oxide ($K_2O+C=CO+K_2$). It decomposes water at ordinary temperatures, liberating hydrogen ($K_2+2H_2O=2KHO+H_2$), which fires spontaneously, owing to the heat of the reaction, potassium hydrate remaining in solution. It fires spontaneously in chlorine, and when brought into contact with bromine. It decomposes H_2S ($H_2S + K_2 = K_2S + H_2$), and combines readily with sulphur and phosphorus.

Uses.—In the laboratory, to expel less strongly electro-positive elements. (*See* Boron, Silicon, etc.)

Compounds of Potassium.—(K=39).

		Salts.	Formula.	Molecular Weight.	Specific Gravity.
1		Potassium hydride	K_2H	79·0	
2	Oxides.	,, oxide (p. 342)	K_2O	94·0	
3		,, dioxide (p. 342)	K_2O_2	110·0	
4		,, peroxide (p. 342)	K_2O_4	142·0	
5		,, hydrate (p. 342)	KHO	56·0	2·1
6	Haloids.	,, chloride (p. 344)	KCl	74·5	1·994
7		,, iodide (p. 344)	KI	166·0	3·056
8		,, bromide (p. 345)	KBr	119·0	2·670
9		,, fluoride (p. 345)	KF	58·0	2·454
10		,, hydric fluoride	KHF_2	78·0	
11		,, fluosilicate (p. 345)	$2KF,SiF_4$	220·7	
12		,, cyanide (p. 345)	KCy	65·1	
13		,, ferrocyanide (p. 345)	K_4FeCy_6	368·4	
14		,, ferricyanide (p. 346)	K_3FeCy_6	329·3	
15	Sulphides.	,, sulphide (p. 346)	K_2S	110·2	
16		,, disulphide (p. 346)	K_2S_2	142·2	
17		,, trisulphide (p. 346)	K_2S_3	174·2	
18		,, tetrasulphide (p. 346)	K_2S_4	206·2	
19		,, pentasulphide (p. 346)	K_3S_5	238·2	
20		,, heptasulphide	K_2S_7 (?)		
21		,, sulph-hydrate (p. 346)	KHS	72·1	
22	Sulphates, etc.	,, sulphate (normal) (p. 347)	K_2SO_4	174·2	2·66
23		,, hydric sulphate (acid) (p. 347)	$HKSO_4$	136·1	2·175
24		,, thiosulphate	$K_2S_2O_3,5H_2O_7$		
25		,, pyrosulphate	$K_2S_2O_7$		
26		,, dithionate	$K_2S_2O_6$		
27		,, sulphite (p. 347)	$K_2SO_3,2H_2O$		
28		,, hydric sulphite (p. 347)	$HKSO_3$		
29		,, pyrosulphite	$K_2S_2O_5$		
30	Phosphates, etc.	,, orthophosphate	K_3PO_4		
31		,, hydric orthophosphate	K_2HPO_4		
32		,, dihydric phosphate	KH_2PO_4		
33		,, pyrophosphate	$K_4P_2O_7,3H_2O$		
34		,, hydric pyrophosphate	$K_2H_2P_2O_7$		
35		,, metaphosphate	KPO_3		
36		,, phosphite	K_2PO_3		
37		,, arsenates	K_3AsO_4 K_2HAsO_4		
38		,, sulpharsenate	K_3AsS_7		
39		,, antimonate	$KSbO_3$		
40		,, sulphantimonate	K_3SbS_4		
41	Carbonates.	,, carbonate (normal) (p. 347)	K_2CO_3	138·2	2·267
42		,, hydric carbonate (p. 348)	$KHCO_3$	100·0	2·052

		Salts.	Formula.	Molecular Weight.	Specific Gravity.
43		Potassium nitrate (p. 348).. ..	KNO_3	101·1	2·100
44		,, nitrite (p. 350).. ..	KNO_2	85·1	
45	Chlorates, etc.	,, chlorate (p. 350) ..	$KClO_3$	122·6	2·326
46		,, amide (p. 351)	KNH_2		
47		,, perchlorate (p. 351)..	$KClO_4$	138·6	
48		,, bromate (p. 351) ..	$KBrO_3$		
49		,, iodate (p. 351).. ..	KIO_3		
50		,, periodate (p. 351) ..	KIO_4		
51		,, selenate	K_2SeO_4		
52		,, tellurate	K_2TeO_4		
53		,, borate (meta)	KBO_2		
54	Tartrates.	,, tartrate (p. 351) ..	$K_2C_4H_4O_6$	226·2	
55		,, hydric tartrate (cream of tartar) (p. 351)..	$KHC_4H_4O_6$	188·1	
56		,, sodic tartrate (Rochelle salt) (p. 351) ..	$KNaC_4H_4O_6$	210·1	
57		,, antimonious tartrate (tartar emetic) (p. 351)	$K(SbO)C_4H_4O_6$	341·1	
58		,, silicate	K_4SiO_4		

COMPOUNDS OF POTASSIUM WITH OXYGEN AND HYDROXYL.

Potassium oxide	K_2O.
Potassium dioxide	K_2O_2.
Potassium peroxide	K_2O_4.
Potassium hydrate	KHO.

(2.) **Potassium Oxide**; *Potassa; Anhydrous potash* ($K_2O=94·0$).

Preparation.—(1.) By heating together potassium and potassium hydrate ($2KHO+K_2=2K_2O+H_2$).

(2.) By fusing a mixture of potassium and potassium peroxide in an atmosphere of nitrogen ($K_2O_4+3K_2=4K_2O$).

(3.) By the spontaneous oxidation of potassium in dry air.

Properties.—A white, deliquescent solid, possessing powerful basic properties. It combines with water, with the evolution of great heat, to form potassium hydrate ($K_2O+H_2O=2KHO$). It fuses at a red heat, and volatilizes at high temperatures.

(3.) **Potassium Dioxide** (K_2O_2). A solution of K_2O_2 is formed when K_2O_4 is dissolved in water.

(4.) **Potassium Peroxide** (K_2O_4) is prepared by fusing potassium in a current of oxygen. Neither the dioxide nor peroxide form corresponding salts with acids.

(5.) **Potassium Hydrate**; *Potash; Caustic potash; Potassa; Potassium hydroxide* ($KHO=56$).

Preparation.—(1.) By boiling calcium hydrate (CaH_2O_2) in an iron vessel with a dilute solution (10 per cent.) of potassium carbonate (*pearlash*) ($K_2CO_3+CaH_2O_2=2KHO+CaCO_3$). [If a strong solution of K_2CO_3 be used, a reverse reaction results ($2KHO+CaCO_3=K_2CO_3+CaH_2O_2$).] The solution of potassium hydrate (KHO), after being decanted from the insoluble calcium carbonate ($CaCO_3$) and the excess of lime, is evaporated down in an iron or silver basin, until it is capable of solidifying on cooling.

(2.) By burning potassium in pure dry oxygen, and treating the oxides so formed with water.

(3.) By igniting a mixture of potassium nitrate (1 part) and copper foil (3 parts) in a copper vessel, and extracting the residue with water.

Properties.—Potassium hydrate is a deliquescent solid, soluble in about half its weight of water with the evolution of heat. Unlike most potassium compounds, it is soluble in alcohol. It has a strong caustic taste, and a nauseous smell. It fuses at a red heat. At a high temperature, it is wholly volatile without decomposition. The water of the hydrate cannot be expelled by heat. It is regarded, therefore as a *potassium hydroxide* (KHO) rather than a *hydrate of potash* (K_2O, H_2O).

Caustic potash has an intensely alkaline reaction, neutralising all acids with the formation of water and the corresponding potassium salt ($KHO+HNO_3=KNO_3+H_2O$). When added to a solution of a metal that possesses an insoluble hydrate, such hydrate will be precipitated ($Fe_2Cl_6+6KHO=Fe_2H_6O_6+6KCl$). It acts energetically on all organic matter. It rapidly absorbs carbonic acid; hence one of its chief laboratory uses. It unites with silica when heated, forming potassium silicate. It decomposes the fixed oils, converting them into soaps; hence its use as a *lye* in soap making.

Tests for purity.—Pure potassium hydrate (1) is perfectly soluble in water and in alcohol; (2) gives no precipitate with *baryta water* (proving the absence of carbonates and sulphates); (3) gives no precipitate with *ammonium oxalate* (proving the absence of lime); (4) gives no precipitate, in a solution neutralized with HNO_3, with *argentic nitrate* (proving the absence of chlorine); (5) gives no precipitate with *ammonium sulphide* (proving the absence of iron, etc.).

Purification.—The potash is dissolved in alcohol, and the clear solution evaporated to dryness. In this way the removal of potassium peroxide, carbonate, sulphate, and chloride, together with the silicates of lime, alumina, iron, and lead, all of which compounds are insoluble in alcohol, may be effected. The solution in water must be preserved in glass free from lead, otherwise the lead oxide will be dissolved.

The liquor potassæ of the B.P. contains 6 per cent. of KHO (sp. gr. 1·058). The specific gravities of solutions of various strength are given in Table V. of the *Appendix.*

HALOID SALTS.

(6.) Potassium Chloride ($KCl = 74 \cdot 5$). *Sources.*—This salt is the predominant salt in flesh. It is obtained from sea-water residue (Balard); also from the ashes of sea-weed ("kelp"); also from the refuse of the beet-sugar manufacture; also as a product of the potassium chlorate manufacture. It is found as a natural product (sylvine), and also with chloride of magnesium in the salt mines of Stassfurth, near Magdeburg (*Carnallite;* $KCl, MgCl_2, 6H_2O$).

Properties.—The salt crystallizes in cubes. Sp. gr. 1·9. It is insoluble in alcohol, but is soluble in three times its weight of water at common temperatures, and in twice its weight at 212° F. (100° C.). It fuses at 1353° F. (734° C.), and is volatile above this temperature. It absorbs the vapor of SO_3, forming $KClSO_3$, which salt is decomposed by water. It is largely used in the nitre manufacture (see page 274). Its laboratory use depends on the insolubility in alcohol of the double salt formed by it with platinic chloride ($2KCl,PtCl_4$), a reaction employed in the quantitative determination of potassium compounds.

(7.) Potassium Iodide ($KI = 166 \cdot 0$).

Preparation.—(1.) (*a.*) Iodine is added to a solution of caustic potash (KHO), potassium iodide (KI) and potassium iodate (KIO_3) being formed. Thus—

$$6KHO + 3I_2 = 5KI + KIO_3 + 3H_2O.$$

Potassium hydrate + Iodine = Potassium iodide + Potassium iodate + Water.

(*β.*) This mixture is then heated, whereby the KIO_3 is reduced to KI, with the evolution of oxygen.

(2.) By dissolving potassium carbonate (K_2CO_3) in hydriodic acid:—

$$K_2CO_3 + 2HI = 2KI + CO_2 + H_2O.$$

Potassium carbonate + Hydriodic acid = Potassium iodide + Carbonic anhydride + Water.

(3.) (*a.*) By digesting iron and iodine in water. A ferrous iodide (FeI_2) and a ferric iodide (Fe_2I_6) are first formed;

(*β*). To the boiling solution of these salts, potassium carbonate is added, carefully avoiding an excess:—

$$FeI_2 + Fe_2I_6 + 4K_2CO_3 = 8KI + Fe_3O_4 + 4CO_2.$$

Ferrous iodide + Ferric iodide + Potassium carbonate = Potassium iodide + Magnetic oxide of iron + Carbonic anhydride.

The Fe_3O_4 is now filtered off, and the solution of KI evaporated to dryness.

(4.) By adding potassium sulphate to barium or calcium iodide.

Properties.—Potassium iodide is a white, crystalline (cubic) solid, somewhat deliquescent, very soluble in water (about 1 in 1) and in alcohol (1 part in 6). Its aqueous solution dissolves iodine. The aqueous solution turns yellow on keeping, from the carbonic acid of the air effecting slight decomposition. It melts at 1175° F. (635° C.). Sp. gr. 3·0. It is decomposed by nitric acid, chlorine, etc.

Tests of purity.—There should be no change on adding hydrochloric acid to its solution. If the solution *turns brown*, potassium iodate (KIO_3) is present; if it *effervesces*, the presence of a carbonate is indicated.

(8.) **Potassium Bromide** ($KBr = 119{\cdot}0$). Its preparation is similar, and its properties closely correspond, to the iodide. It is soluble in water—1 in 2, at 60° F.; 1 in 1, at 212° F. It is also soluble in alcohol. Sp. gr. 2·69. It melts at 1292° F. (700° C.).

(9.) **Potassium Fluoride** (KF) is prepared by neutralizing HF with KHO. It is deliquescent, and its solution dissolves glass. It forms numerous double fluorides.

(11.) **Potassium Fluosilicate** (or *silico-fluoride*) ($2KF,SiF_4$). This is the most insoluble of the potash salts. It is formed as a gelatinous precipitate, when hydrofluosilicic acid ($2HF,SiF_4$) is added to a solution of a potassium salt. When dry it has the appearance of an earthy-looking powder.

(12.) **Potassium Cyanide** (KCy).

Preparation.—By fusing a mixture of potassium carbonate and potassium ferrocyanide:—

$$2K_4FeCy_6 + 2K_2CO_3 = 10KCy + 2KCyO + Fe_2 + 2CO_2.$$

$2K_4FeCy_6$	+	$2K_2CO_3$	=	$10KCy$	+	$2KCyO$	+	Fe_2	+	$2CO_2$.
Potassium ferrocyanide	+	Potassium carbonate	=	Potassium cyanide	+	Potassium cyanate	+	Iron	+	Carbonic anhydride.

Properties.—A white, deliquescent, peculiar-smelling, alkaline salt, freely soluble both in water and in alcohol. It easily decomposes, liberating hydrocyanic acid (HCy). It melts at a low temperature, when it acts as a powerful *reducing* agent, owing to the ease with which it forms a cyanate ($KCyO$). Hence its use as a flux ($PbO + KCy = KCyO + Pb$).

Its solution dissolves the insoluble silver salts; hence its use in photography and in electro-plating.

(13.) **Potassium Ferrocyanide,** *Yellow prussiate* ($K_4FeCy_6,3H_2O$).

Preparation.—By heating a mixture of potassium carbonate (K_2CO_3), iron, and nitrogenized organic matter. The fused mass is lixiviated (dissolved in water), and the clear solution crystallized.

Properties.—The salt has a yellow color, is permanent in air, and is decomposed by heat. It is insoluble in alcohol, but is soluble in water (1 in 4 at 60° F., and 1 in 2 at 212° F.).

It is used as a test re-agent, as a case-hardener, and in the manufacture of Prussian blue.

(14.) Potassium Ferricyanide, *Red prussiate* ($K_3Fe'''Cy_6$).

Preparation.—By passing chlorine (avoiding an excess) through a cold dilute solution of potassium ferrocyanide until it turns red.

Properties.—It is decomposed by an excess of chlorine, and by oxidizing agents.

COMPOUNDS OF POTASSIUM AND SULPHUR.

Potassium sulphide	K_2S.
Potassium disulphide	K_2S_2.
Potassium trisulphide	K_2S_3.
Potassium tetrasulphide	K_2S_4.
Potassium pentasulphide	K_2S_5.
Potassium heptasulphide	K_2S_7.
Potassium sulphhydrate	KHS.

(15.) Potassium Sulphide (K_2S).

Preparation.—(1.) By igniting K_2SO_4 with carbon in a current of hydrogen ($K_2SO_4 + 4C = K_2S + 4CO$).

(2.) By the action of KHO on KHS ($KHO + KHS = K_2S + H_2O$).

Colorless crystals (crystals = $K_2S,5H_2O$) very soluble in water, the solution dissolving the sulphides of tin, antimony, and arsenic. On exposure to air in solution it absorbs oxygen, forming a hydrate and a thiosulphate ($2K_2S + H_2O + 2O_2 = K_2S_2O_3 + 2KHO$).

(16.) Potassium Disulphide (K_2S_2), is an orange-colored, fusible solid. Prepared by exposing KHS to air.

(17.) Potassium Trisulphide (K_2S_3).

Preparation.—By passing the vapor of CS_2 over ignited potassium carbonate :—

$$\underset{\substack{\text{Potassium}\\\text{carbonate}}}{2K_2CO_3} \underset{+}{+} \underset{\substack{\text{Carbon}\\\text{disulphide}}}{3CS_2} \underset{=}{=} \underset{\substack{\text{Potassium}\\\text{trisulphide}}}{2K_2S_3} \underset{+}{+} \underset{\substack{\text{Carbonic}\\\text{oxide}}}{4CO} \underset{+}{+} \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{CO_2.}$$

The "*hepar sulphuris*," or "*liver of sulphur*" (*potassa sulphurata*), is a compound of $3K_2S_3$ and K_2SO_4, and is prepared by fusing sulphur with potassium carbonate:—

$$\underset{\text{Potassium carbonate}}{4K_2CO_3} \underset{+}{+} \underset{\text{Sulphur}}{5S_2} \underset{=}{=} \underbrace{K_2SO_4 + 3K_2S_3}_{\text{Liver of sulphur}} \underset{+}{+} \underset{\text{Carbonic anhydride.}}{4CO_2.}$$

(19.) Potassium Pentasulphide, *Potassium Persulphide* (K_2S_5).

Preparation.—Either by the fusion of a solid sulphide, or by boiling a solution of a sulphide with an excess of sulphur.

Properties.—A deliquescent solid, forming when dissolved a deep yellow solution.

(21.) Potassium Sulph-hydrate, or *Potassium Hydric Sulphide* (KHS = 72·1). The analogue of KHO.

Preparation.—(*In Solution.*) By saturating potassium hydrate with sulphuretted hydrogen ; or (as a *solid*) by heating potassium or potassium carbonate in H_2S :—

KHO	+	H_2S	=	KHS	+	H_2O.
Potassium hydrate	+	Sulphuretted hydrogen	=	Potassium sulph-hydrate	+	Water.

The solution turns yellow on exposure to air, and freely absorbs oxygen ($4KHS + O_2 = 2K_2S_2 + 2H_2O$).

All the sulphides have an alkaline reaction, and a sulphuretted hydrogen odor. They all liberate sulphuretted hydrogen when treated with acids. On adding an acid this distinction is to be noted ; that—

(*α.*) With K_2S and KHS, *sulphuretted hydrogen* is evolved, but no sulphur precipitated ($KHS + HCl = KCl + H_2S$).

(*β.*) With the other sulphides, in addition to *sulphuretted hydrogen* being evolved, *finely-divided white sulphur* is precipitated ($K_2S_3 + 2HCl = 2KCl + H_2S + S_2$).

The higher sulphides, on exposure to air, become white from the formation of potassium thiosulphate ($K_2S_2O_3$), the excess of sulphur being liberated.

OXYSALTS OF POTASSIUM.

(22.) **Potassium Sulphate** (normal salt ; $K_2SO_4 = 174{\cdot}2$).

Properties.—The crystals are six-sided prisms, insoluble in alcohol, soluble in water (1 in 12 cold—1 in 4 boiling). The solution is neutral. It is obtained as a by-product from the mother liquors formed both in the preparation of carbonate of potash from wood ashes, and in the manufacture of soda from kelp, etc. The crystals decrepitate when heated, and melt unchanged at a red heat.

(23.) **Potassium Hydric Sulphate;** *Potassium Bisulphate* (acid salt ; $HKSO_4 = 136{\cdot}1$). This salt is a residuary product of the nitric acid manufacture. The crystals are rhomboidal tables. Fuses at 392° F. (200° C.). When dissolved in a great excess of water, the normal salt crystallizes out. Heated above 200° C. it becomes *potassium pyrosulphate* ($K_2S_2O_7$), which at 1112° F. (600° C.) becomes the normal salt, whilst oxygen, sulphuric and sulphurous anhydrides are evolved.

(27.) **Potassium Sulphite** ($K_2SO_3,2H_2O$) is prepared by expelling the CO_2 from a solution of K_2CO_3 by SO_2. When heated it yields a sulphate.

(28.) **Potassium Hydric Sulphite** ($KHSO_3$) emits an odor of SO_2. By exposure to air it becomes a sulphate.

(41.) **Potassium Carbonate** ($K_2CO_3 = 138{\cdot}2$). *Preparation.*—(1.) Wood-ashes (which contain potassium carbonate, sulphate and chloride) are first of all mixed with water. The solution is then evaporated down until it begins to crystallize. The clear liquor containing the more soluble potassium carbonate (the impurities having crystallised out), is then poured off and boiled down in an iron-pot (hence the term *pot-ash*), and the residue calcined. This is again dissolved in water and the solution evaporated down, this residue being known as "American ash" or "pearl-ash," which contains about 80 per cent. of the carbonate.

(NOTE.—The potassium is not present in the plant as potassium carbonate, but in combination with various organic acids. These salts are decomposed by heat, the hydrogen and excess of carbon passing off as H_2O and CO_2. Further, the younger the plant, the larger the yield of potash.)

(2.) By deflagrating a mixture of cream of tartar and nitre.

(3.) It may also be obtained from the sulphate by a process similar to the Leblanc process (p. 357).

(4.) A pure carbonate may be obtained by the careful crystallization of the residue remaining after cream of tartar ($KHC_4H_4O_6$) has been heated to redness in a platinum crucible.

Properties.—Potassium carbonate (sp. gr. 2·2) is a white, deliquescent salt, crystallizing in oblique rhombic octahedra. It is insoluble in alcohol, but soluble in water (1 in 1 aq.), the solution having an alkaline reaction. From the solution it crystallizes as $2K_2CO_3,3H_2O$, which dried at 212° F. (100° C.) becomes K_2CO_3,H_2O and at a higher temperature K_2CO_3. It melts at a red heat [1540° F. (838° C.)], and is slightly volatile at a higher temperature. When sand (SiO_2) is added to the melted salt, CO_2 escapes, a potassium silicate being formed.

(42.) Potassium Hydric Carbonate; *Acid Potassium Carbonate, Bicarbonate of Potash* ($KHCO_3 = 100·1$).

Preparation.—By passing CO_2 through a cold solution of potassium carbonate (K_2CO_3) ($K_2CO_3 + CO_2 + H_2O = 2KHCO_3$).

Properties.—A neutral body, crystallizing in right rhombic prisms, which are permanent in air. It is less soluble in water than K_2CO_3 (1 in 4), the solution being feebly alkaline. It fuses when heated, forming the normal salt ($2KHCO_3 = K_2CO_3 + H_2O + CO_2$).

(43.) Potassium Nitrate, *Nitre* or *Saltpetre* ($KNO_3 = 101·1$), is formed naturally, as an efflorescence, on the soil in India, and is prepared artificially in the nitre-plantations of Sweden (*see* page 320). "Converted nitre" is formed from sodium nitrate by the action upon it of potassium chloride. The sodium chloride is about equally soluble in hot and cold water, whereas the potassium nitrate crystallizes out as the water cools.

Properties.—A white crystalline solid. Sp. gr. 2·1. It is dimorphous, crystallizing both in rhombohedra and in six-sided prisms. It is insoluble in alcohol, but is soluble in cold water in the proportion of 1 in 3·5, and in boiling water as 3 in 1 of water. The solution is attended with great absorption of heat. When heated to 674° F. (358° C.) it melts, the fused mass forming when cast into shape "*sal prunelle balls.*" When potassium nitrate is heated to redness, oxygen is evolved, and a potassium nitrite (KNO_2) formed; but when heated *above* this temperature, the nitrite itself is decomposed into O, N, and K_2O. Hence its value as an oxidizing agent. When thrown on hot coal, the nitrate deflagrates. Paper saturated with a solution of the salt and dried, constitutes touch-paper. Potassium nitrate is used in the gunpowder manufacture.

Gunpowder.

Composition.—A mixture of nitre, charcoal and sulphur in the following proportions :—

	English and Austrian.	Prussian.	Chinese.	French.
Nitre	75	75·0	75·7	75·0
Charcoal	15	13·5	14·4	12·5
Sulphur	10	11·5	9·9	12·5
	100·0	100·0	100·0	100·0

MATERIALS.

Nitre.—Sodium nitrate is never used in the manufacture of gunpowder on account of its being far more hygroscopic than potassium nitrate, and possessing much less powerfully oxidizing properties. It is of importance that the nitre should be free from sodium and potassium chlorides, as their presence would render the powder liable to become damp.

Charcoal.—Light wood charcoal, such as that from the alder and willow, is the form best adapted for the manufacture of powder, owing to its very ready combustibility.

Sulphur.—The sulphur commonly used is *distilled,* and not *sublimed* sulphur. On mixing a quantity of the sulphur with water, the solution should be barely acid to litmus, proving the absence of oxidised products. It should, when burnt, leave no ash. The *distilled* sulphur is the electro-negative or soluble form, but the *sublimed* sulphur contains a considerable quantity of the positive or insoluble variety. Hence the superiority of the distilled over the sublimed.

Preparation.—The materials are severally finely powdered. They are now mixed in "incorporating mills," a small quantity of water being added. The mixture is then submitted to hydraulic pressure, and the cake so formed "granulated" in order to permit perfect penetration of flame. The grains are sorted according to size, and dried at about 125° F. If the powder be mixed with a sufficient quantity of incombustible material, like sand, to isolate the grains, it becomes incombustible, whilst if it be very finely powdered, it merely burns and does not explode.

Properties.—Gunpowder is an angular grey solid, absorbing from 0·5 to 1·0 per cent. of moisture when exposed to the air. It explodes at about 550° F. (232° C.). It fires with difficulty by actual flame. It should leave no residue, and should not set light to the piece of paper on which it is exploded.

Decomposition.—When gunpowder is fired, the charcoal burns at the expense of the oxygen of the nitre, forming CO_2 and CO. Some of the CO_2 thus formed immediately combines with the potash to form K_2CO_3. The sulphur, which is added to increase combustibility, becomes oxidized to SO_3, which, combining with potash, forms K_2SO_4. Hence *the solids* formed by the explosion of gunpowder (equal to about 57 per cent. by weight of the gunpowder used) are potassium sulphate and potassium carbonate, and the *gases* (equal to about 43 per cent. by weight of the powder used) are nitrogen, carbonic oxide, and carbonic anhydride :—

$$\underset{\text{Potassium nitrate}}{4KNO_3} + \underset{\text{Carbon}}{C_4} + \underset{\text{Sulphur}}{S} = \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Potassium carbonate}}{K_2CO_3} + \underset{\text{Nitrogen}}{N_4} + \underset{\text{Carbonic anhydride}}{2CO_2} + \underset{\text{Carbonic oxide.}}{CO.}$$

Other bodies, however, such as K_2S, H_2S and CH_4 are also formed.

Theory of gunpowder explosions.—The nitrogen and the carbonic anhydride set free by firing the powder, occupy at 0° C. and standard pressure 280 times the volume of the original powder ; but this volume of gas is again expanded to as much, probably, as five times the normal bulk by the heat developed.

A cubic inch of powder yields about 280 cubic inches of gas at normal temperature and pressure. The high temperature of explosion (4000° F.), if the powder be exploded in a space which it entirely fills, increases the pressure to about 6,400 atmospheres (42 tons to the square inch. By the explosion of 1 lb. of powder we could raise 1 ton 480 feet high. (Dupré.)

(44.) **Potassium Nitrite** (KNO_2). This is prepared by heating potassium nitrate (*q. v.*). It is a white, crystalline, deliquescent salt.

(45.) **Potassium Chlorate** ($KClO_3 = 122·6$). *Preparation.* (1.) By passing chlorine through a hot solution of potassium hydrate :—

$$\underset{\text{Potassium hydrate}}{6KHO} + \underset{\text{Chlorine}}{3Cl_2} = \underset{\text{Potassium chloride}}{5KCl} + \underset{\text{Potassium chlorate}}{5KClO_3} + \underset{\text{Water.}}{3H_2O.}$$

The chlorate crystallizes out from the concentrated liquor, whilst the potassium chloride remains in solution owing to its greater solubility.

(2.) By passing chlorine, either (*a.*) into a solution of potassium carbonate and calcium hydrate (5 mols. of CaH_2O_2 to 1 mol. of K_2CO_3), or (*β.*) through milk of lime (whereby a calcium chlorate ($Ca2ClO_3$) and a calcium chloride ($CaCl_2$) are formed), to which potassium chloride is afterwards added.

$$
\begin{array}{lcccccccccccccc}
(\alpha.) & K_2CO_3 & + & 5CaH_2O_2 & + & 6Cl_2 & = & 2KClO_3 & + & 5CaCl_2 & + & 5H_2O & + & CO_2. \\
& \text{Potassium} & + & \text{Calcium} & + & \text{Chlorine} & = & \text{Potassium} & + & \text{Calcium} & + & \text{Water} & + & \text{Carbonic} \\
& \text{carbonate} & & \text{hydrate} & & & & \text{chlorate} & & \text{chloride} & & & & \text{anhydride.}
\end{array}
$$

$$
\begin{array}{lccccccc}
(\beta.) & (Ca2ClO_3) & + & 2KCl & = & CaCl_2 & + & 2KClO_3. \\
& \text{Calcium chlorate} & + & \text{Potassium chloride} & = & \text{Calcium chloride} & + & \text{Potassium chlorate.}
\end{array}
$$

The chlorate is now separated by crystallization, the $CaCl_2$ being a very much more soluble salt than the chlorate.

Properties.—Potassium chlorate (Sp. gr. 2·32) is a white crystalline solid (six-sided prisms). It is not very soluble in water (1 in 16 of cold, 1 in 2 of boiling water). It melts at 633° F. (334° C.), and gives off oxygen at 680° F. (360° C.), the residue consisting of *potassium perchlorate* ($KClO_4$) and *potassium chloride* ($2KClO_3 = KClO_4 + KCl + O_2$), the perchlorate at a greater heat being resolved into potassium chloride and oxygen. It is a powerful oxidizing agent.

(46.) **Potassium Amide** (KNH_2) is prepared by heating potassium in a current of dry ammonia. It is decomposed by water ($KNH_2 + H_2O = NH_3 + KHO$). Heated in vacuo, it forms NH_3 and potassium nitride (K_3N). It inflames spontaneously in air.

(47.) **Potassium Perchlorate** ($KClO_4 = 138{\cdot}6$). (*See above.*) Sp. gr. 2·52. Gives off oxygen at 752° F. (400° C.). Soluble in 70 parts of cold, and 6 parts of boiling water. Insoluble in alcohol.

(48.) **Potassium Bromate** ($KBrO_3$) is prepared by passing chlorine into an aqueous solution of bromine and potassium carbonate ($6K_2CO_3 + 5Cl_2 + Br_2 = 2KBrO_3 + 10KCl + 6CO_2$).

(49.) **Potassium Iodate** (KIO_3) is prepared by passing chlorine through water containing iodine in suspension, ICl being formed. Potassium chlorate is then added to the mixture ($ICl + KClO_3 = KIO_3 + Cl_2$).

(50.) **Potassium Periodate** (KIO_4) is prepared by passing chlorine through a solution of potassium iodate in caustic potash. A basic salt is precipitated, which, dissolved in dilute nitric acid, and the solution evaporated to dryness, leaves the normal salt $KIO_4,3H_2O$. At 527° F. (275° C.) the periodate is converted into an iodate and oxygen, and at higher temperatures may be completely reduced to the condition of an iodide.

(54.) **Potassium Tartrate** ($K_2C_4H_4O_6$) is prepared by boiling together cream of tartar and potassium carbonate.

(55.) **Hydric Potassium Tartrate**; *Potassium Bitrartrate; Cream of Tartar* ($KHC_4H_4O_6$).—This is one of the most insoluble of potash salts. It is found deposited in casks used for the storage of wines.

(56.) **Sodium Potassium Tartrate,** *Rochelle salt* ($KNaC_4H_4O_6$), is prepared by boiling together cream of tartar and sodium carbonate.

(57.) **Potassium Antimonious Tartrate,** *Tartar emetic* ($K(SbO), C_4H_4O_6$), is prepared by boiling together cream of tartar ($KHC_4H_4O_6$) and antimonious oxide (Sb_2O_3).

REACTIONS OF POTASSIUM COMPOUNDS.

[All potassium salts are white, unless the acid be colored.]

(1.) Gives violet-colored flame, which appears red when seen through cobalt blue glass.

(2.) *Spectrum.*—Two lines (Kα in red and Kβ in violet), both being coincident with the lines of the solar spectrum.

(3.) *Platinic Chloride* ($PtCl_4$) in HCl solution, gives a yellow ppt. ($PtCl_4$, 2KCl), sparingly soluble in water, insoluble in alcohol and ether, and soluble in a solution of potassium hydrate.

[Heated to redness, potassium platinic chloride evolves chlorine, leaving KCl and metallic platinum.]

(4.) *Hydrofluosilicic Acid* (H_2SiF_6), gives a gelatinous ppt. (K_2SiF_6), insoluble in alcohol.

(5.) *Tartaric Acid*, in excess, gives a white ppt. in strong solutions of hydric potassium tartrate ($KHC_4H_4O_6$).

SODIUM (Na_2).

Na=23. *Monad* (Na'Cl). *Specific gravity* 0·972. *Fuses at* 97·6° F. (207·7° C.). *Boils at about* 1652° F. (900° C.). *Specific heat* 0·293.

History.—Discovered by Davy (1807) by the electrolysis of NaHO.

Natural History.—It does not occur free in nature. Combined it is found in animals, in vegetables ("barilla"), and in minerals. It occurs naturally as a chloride (in rock salt, etc.), carbonate, nitrate (in Chili saltpetre), sulphate, borate, iodide (in sea plants, etc.), and silicate (in sodalite and albite).

Preparation.—Its preparation is similar to that of potassium (*q. v.*, p. 340), viz.: (1) (*manufacturing process*), by igniting a mixture of sodium carbonate and carbon ; (2) by the electrolysis of NaHO ; and (3) by the ignition of a mixture of sodium hydrate and metallic iron.

Properties.—(α.) *Physical.* A soft silvery-white metal. At —4° F. (—20° C.) it is hard. It may be obtained in crystals by fusion in coal-gas, the liquid portion being afterwards decanted. It volatilizes and may be distilled even more readily than potassium, and burns with a *yellow* flame. Its spectrum consists of a double yellow line at D.

(β.) *Chemical.* Sodium oxidizes rapidly in air, and burns when heated. Its properties are similar to, but less energetic than, potassium. It decomposes water at ordinary temperatures, forming NaHO and liberating hydrogen. It fires in water above 140° F. (60° C.), but not if the water be cold unless thickened with starch or other material. It is not acted upon either by chlorine or bromine, except in the presence of moisture.

Uses.—It is employed for the extraction of metallic aluminium and magnesium. (*See* Aluminium *and* Magnesium.) It is also used to extract gold and silver from their ores. It is employed in the laboratory as a source of nascent hydrogen.

Compounds of Sodium (Na = 23).

		Names.	Formula (General).	Molecular Weight of Anhydrous Salts.	Specific Gravity of Crystals.
1		Sodium hydride (p. 353)	Na_4H_2	94	0·959
2	Oxides.	„ oxide (soda) (p. 354) ..	Na_2O	62	
3		„ dioxide (p. 354)	Na_2O_2	78	
4		„ hydrate (p. 354)	$NaHO$	40	2·13
5	Haloids.	„ chloride (p. 355)	$NaCl$	58·5	2·24
6		„ iodide (p. 356)	NaI	150	3·45
7		„ bromide (p. 356)	$NaBr$	103	3·08
8		„ fluoride (p. 356)	NaF		
9		„ fluosilicate..	$2NaF,SiF_4$		
10		„ sulphate (p. 356)	$Na_2SO_4,10H_2O$	142	1·469
11		„ sulphides (like Potassium, *q. v.*)			
12	Sulphates, etc.	„ hydric sulphate (p. 357) ..	$NaHSO_4$	120	2·742
13		„ sulphite (p 357)	$Na_2SO_3,7H_2O$	126	1·736
14		„ hydric sulphite (p. 357) ..	$NaHSO_3,4H_2O$	104	
15		„ thiosulphate (p. 357) ..	$Na_2S_2O_3 5H_2O$	158	1·672
16		„ pyrosulphite	$Na_2S_2O_7$		
17		„ dithionate	$Na_2S_2O_6$		
18	Phosphates.	„ phosphate (p. 361)	$Na_3PO_4,12H_2O$	164	1·618
19		„ hydric phosphate (p. 361)	$Na_2HPO_4,12H_2O$	142	1·525
20		„ dihydric phosphate ..	$NaH_2PO_4H_2O$	120	
21		„ pyrophosphate (p. 362) ..	$Na_4P_2O_7,10H_2O$	266	1·836
22		„ metaphosphate (p. 362) ..	$NaPO_3$	102	30·39
23		„ hydric potassium phosphate	$HKNaPO_4,7H_2O$		
24	Carbonates.	„ carbonate (p. 357)	$Na_2CO_3 10H_2O$	106	1·423
25		„ hydric carbonate (p. 360)	$NaHCO_3$	84	2·192
26		„ potassic carbonate (p. 360)	$KNaCO_3,6H_2O$		
27		„ sesquicarbonate (p. 360) ..	$(Na_2CO_3,2NaHCO_3,2H_2O)$		
28		„ nitrate (p. 360)..	$NaNO_3$	85	2·26
29		„ nitrite (p.360)	$NaNO_2$		
30		„ chlorate (p. 360)	$NaClO_3$		
31		„ perchlorate (p. 361)	$NaClO_4$		
32		„ bromate (p. 361)	$NaBrO_3$		
33		„ iodate (p. 361)	$NaIO_3$		
34		„ periodate (p. 361)	$NaIO_4$		
35		„ selenate	$Na_2SeO_4,10H_2O$		
36		„ tellurate	Na_2TeO_4		
37		„ arsenate	$Na_3AsO_4\cdot 12H_2O$		
38		„ hydric arsenate	$Na_2HAsO_4\cdot 12H_2O$ $NaH_2AsO_4H_2O$		
39		„ silicate (p. 362)	$Na_2SiO_3\cdot 8H_2O$		
40		„ sulpharsenate	Na_3AsS_4		
41		„ sulphantimonate	$Na_3SbS_4,9H_2O$		
42		„ borate (borax) (p. 361) ..	$Na_2O,2B_2O_3,10H_2O$	202	1·73
43		„ metaborate	$NaBO_2,4H_2O$		
44		„ amide..	$NaNH_2$		

(1.) **Sodium Hydride** (Na_4H_2) is prepared by heating sodium in dry hydrogen to a temperature between 572° F. and 752° F. (300° and 400° C.). A silvery body. Sp. gr. 0·959. Dissociates in air at 788° F. (420° C.).

Compounds of Sodium with Oxygen, etc.

Sodium oxide	Na_2O.
Sodium dioxide	Na_2O_2.
Sodium hydrate	NaHO.

(2.) Sodium Oxide; *Soda* (Na_2O).

Preparation.—By burning the metal in oxygen or in dry air. (The product contains more or less Na_2O_2.) *Properties.*—A yellowish white body, very deliquescent, forming NaHO when dissolved in water.

(3.) Sodium Dioxide (Na_2O_2). *Preparation.*—By heating sodium to 392° F. (200° C.) in a current of dry air. *Properties.*—It is a white solid when cold, becoming yellow when heated. On heating a solution of the salt in water, oxygen is expelled.

(4.) Sodium Hydrate; *Caustic Soda; Soda; Sodium hydroxide* (NaHO). [For preparation *see* Potassium Hydrate, to which it is in all respects similar, page 342.]

Preparation.—(*Commercial.*) Caustic soda is largely prepared from the *red liquor* of the alkali works (*see* page 358). The solution of the black ash is concentrated to 1·5 specific gravity, the carbonate, sulphate and chloride of sodium, crystallizing out in course of evaporation. The resulting liquor (*i.e.*, the liquor remaining after the deposited crystals have been removed) constitutes "*red liquor*," which retains in solution the sodium hydrate, owing to its greater solubility. Certain other compounds are present in small quantity, such as the sulphides of iron and sodium, to which the peculiar red color of the solution is due. The hot liquor is then treated, either with sodium nitrate and a current of air, or with sodium nitrate only, in order to oxidize the sulphides present, ferric oxide being thrown down. The clear solution is then evaporated and the sodium hydrate obtained as a fused mass.

Kryolite ($3NaF,AlF_3$) is also employed in the preparation of sodium hydrate by effecting its decomposition with calcium hydrate.

Properties.—Sodium hydrate is a white solid. Sp. gr. 2·13. It is soluble in two and a-half parts of water at ordinary temperatures. It fuses below redness, and is volatile at a white heat. On exposure to air, it first becomes liquid by absorbing water, but afterwards dries up by the absorption of carbonic anhydride. It is very soluble in water and in alcohol, its solution absorbing CO_2 from air. If a strong aqueous solution of the hydrate be exposed to a freezing mixture, it deposits crystals of $2NaHO,7H_2O$.

It acts rapidly on organic structures. It is largely used in the manufacture of *hard soap* (*i.e.*, caustic soda and fat or oil), of *marine soap* (*i.e.*, caustic soda and cocoa-nut oil), etc.

For the specific gravity of solutions of different strength, *see* Table VI. in Appendix.

Haloid Salts.

(5.) **Sodium Chloride;** *Common salt; Muriate of soda* (NaCl).

Natural History.—(1.) From *beds of "rock salt,"* such as are found at Northwich, Cardona, Wielitzka, etc. The red tint of ordinary rock salt is due to the presence of iron. The perfectly white crystallized specimens occasionally found are known as "*sal gem.*"

(2.) *Sea water.*—The salt obtained from this source is called *Bay Salt.* The solution remaining after the extraction of the salt is called "*bittern.*"

Every 1000 parts of sea-water (*see* p. 247) contains about :—

29·0 parts of chloride of sodium (=4 ozs. of salt per gallon, or 1 bushel in 300 to 350 gallons of water).
0·5 „ „ chloride of potassium.
3·0 „ „ chloride of magnesium.
2·5 „ „ sulphate of magnesium.
1·5 „ „ sulphate of lime.

(3.) *Salt springs;* also *rivers, lakes, soils,* etc.

Preparation.—(1.) In the case of salt mines, it has been found more economical first to let water into the mine, and then pump up the saturated solution, than to raise the solid salt itself from the mine. The salt is crystallised from its solution, the details of the process varying in different countries :—

(α.) Sometimes the water is evaporated off in shallow basins.

(β.) Sometimes the brine, if dilute, is first of all concentrated by allowing it to flow several times from a height over brushwood freely exposed to the air (*graduation*), its further concentration being effected by heat after the solution has attained a gravity of 1·14 (France and Germany).

(γ.) In *cold* climates the salt water is run into open reservoirs, and allowed to freeze. The ice, which contains very little salt, is removed, the concentrated solution of salt remaining being finally evaporated to dryness (Russia).

(δ.) In *hot* climates the sea water is allowed to evaporate spontaneously in shallow reservoirs, when what is called "*bay salt*" is deposited. The salt prepared from sea-water always contains magnesium chloride, which may to a certain extent be separated from the sodium chloride by exposure to air and by washing, owing to the greater deliquescence of the magnesium chloride. The liquor remaining after the sodium chloride has been removed is called "bittern," and is employed as a source of magnesia and of bromine.

(2.) Sodium chloride is formed when sodium is burnt in chlorine.

Properties.—Common salt is a crystalline (cubic), non-deliquescent solid. The presence of a minute trace of urea in the solution makes the salt to crystallize in octahedra. Below 14° F. (—10° C.) it crystallizes from water as $NaCl,2H_2O$. The presence of magnesium chloride renders it deliquescent. A clear colorless specimen of salt is *diathermanous*, that is, it allows the *heat* rays to pass as well as the *light* rays. [Water is non-diathermanous, glass holding an intermediate position in this respect between water and salt.] It is insoluble in absolute alcohol, but is soluble in dilute alcohol. It is about equally soluble in water at all temperatures (1 in 3), a saturated solution having a specific gravity of 1·205. The crystals decrepitate when heated. At a bright red heat 1421·6° F. (772° C.) the crystals fuse, and at a stronger heat the salt vaporizes.

Uses.—It is used for dietetic and culinary purposes, as *e.g.*, for curing meats, owing to its antiseptic action. It is also used in agriculture, in earthenware glazing, etc. It is largely employed in the carbonate of soda manufacture.

(6.) **Sodium Iodide** (NaI), (7.) **Bromide** ($NaBr$), and (8.) **Fluoride** (NaF). (*Vide* Potassium Iodide, Bromide, and Fluoride, to which the sodium compounds are closely analogous, page 344.)

The Sulphides.

See Sulphides of Potassium, to which the sulphides of sodium are analogous (page 346.)

SODIUM OXY-SALTS.

(10.) **Sodium Sulphate**; *Glauber's salt* ($Na_2SO_4,10H_2O = 142 + 180 = 322$).

Natural History.—Occurs naturally in many waters; also in certain minerals, as Thénardite, Glauberite ($Na_2SO_4, CaSO_4$) etc.; also as a common efflorescence on brick walls, etc.

Preparation.—The salt is formed in the first stage of the sodium carbonate manufacture by the action of sulphuric acid on common salt (*see* page 357), the product being commonly known as "*salt cake.*" It also constitutes a bye-product in the nitric acid manufacture (page 141).

Properties.—A colorless salt, having a bitter taste and a purgative action. Sp. gr. 1·46. It crystallizes in oblique rhomboid prisms, or in forms derived therefrom. The crystals are efflorescent, giving off the whole of their water at common temperatures. The salt melts in its own water of crystallization when heated to 91·4° F. (33° C.). The anhydrous salt melts at 1580° F. (860° C.).

Its solubility in water is remarkable. 100 parts of water dissolves 9 parts of the anhydrous salt at 50° F., and 55 parts at 85° F., but only 43 parts at 212° F.

(α.) The solubility of the salt Na_2SO_4 decreases from 64·2° F. (17·9° C.) to 217·5° F. (103·1° C.).

(β.) The solubility of the salt $Na_2SO_4, 10H_2O$ increases up to 93·1° F. (33·9° C.) (100 of water dissolve 117·9 parts of this salt).

A hot saturated solution, on being cooled without disturbance and out of contact with air, does not crystallize. On admission of air, however, or if a minute crystal of the salt be introduced into the cold solution, immediate crystallization will be effected, a rise of temperature resulting.

Sodium sulphate is soluble in hydrochloric acid, its solution (8 of the sulphate in 5 parts of the acid), being accompanied by great cold. Hence its use as a freezing mixture.

(12.) **Sodium Hydric Sulphate**; *Acid sodium sulphate; Bisulphate of soda* ($NaHSO_4 = 120$).

Preparation.—By adding seven parts of sulphuric acid to ten parts of the anhydrous normal salt, and evaporating.

Properties.—A non-deliquescent and very soluble salt, having an acid reaction. Heated above the fusing point, it forms sodium pyrosulphate ($Na_2S_2O_7$), which at a still higher temperature becomes the normal salt with evolution of SO_3.

(13.) **Sodium Sulphite** (Na_2SO_3, $7H_2O$).

Preparation.—By passing SO_2 over crystals of Na_2CO_3.

Properties.—The salt crystallizes in oblique prisms, which are efflorescent, and fuse at 113° F. (45° C.). It is soluble in water (1 in 4), the solution having an alkaline reaction. It evolves sulphurous acid when treated with HCl or with H_2SO_4. It is used as a bleaching agent, and as an "antichlor."

(14.) **Sodium Hydric Sulphite,** *Acid sulphite, Bisulphite* ($NaHSO_3$). This salt becomes a sulphite spontaneously by exposure to air.

(15.) **Sodium Thiosulphate** (*see* page 318).

(24.) **Sodium Carbonate** (neutral); *Common washing soda; Soda; Scotch soda*—(Na_2CO_3, $10H_2O = 106 + 180 = 286$).

Natural History.—Found in the Egyptian and Hungarian soda lakes, in the volcanic springs of Iceland, in the ashes of sea-plants, etc.

Preparation.—(1.) Before the year 1823, this salt was prepared from the ashes of sea-weed, known as "*kelp*," "*barilla*," or "*varec*," one-fourth the weight of which consists of sodium carbonate. The kelp was mixed with water, and the clear solution concentrated by heat. The sodium carbonate crystallized out first, leaving the iodine compounds in solution, owing to their much greater solubility.

(2.) *Process of Leblanc.*—*Soda-ash process* (used since 1823). This process may be described in three stages as follows:—

(*a.*) A mixture of common salt and oil of vitriol is first heated in cast iron pans, whereby solid sodium sulphate is formed ["*salt cake*"]—

$$\underset{\text{Sodium chloride}}{2NaCl} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Hydrochloric acid.}}{2HCl.}$$

[The use of sulphurous acid, steam, and air, was suggested by

Hargreave in place of H_2SO_4 [$2NaCl + H_2O + SO_2 + O = Na_2SO_4 + 2HCl$].

(β.) The salt cake thus formed is now mixed with limestone and small coal, and heated in the reverberatory furnace. The following changes occur:—(1.) The carbon reduces the sodium sulphate to sodium sulphide, carbonic anhydride being set free ($Na_2SO_4 + C_2 = Na_2S + 2CO_2$). (2.) The carbon acting on the calcium carbonate, sets free carbonic oxide and lime ($CaCO_3 + C = 2CO + CaO$). (3.) The lime reacts on the sodium sulphide in the presence of carbonic anhydride, producing sodium carbonate (which is soluble), and calcium sulphide which is insoluble) ($Na_2S + CaO + CO_2 = Na_2CO_3 + CaS$).

The reaction in full may be thus stated:—

Na_2SO_4	+	$4C$	+	$CaCO_3$	=	CaS	+	$4CO$	+	Na_2CO_3.
Sodium sulphate	+	Carbon	+	Calcium carbonate	=	Calcium sulphide	+	Carbonic oxide	+	Sodium carbonate.

The black mass formed constitutes what is commonly known as "*black ash*" or "*ball soda*," and consists of the excess of chalk and coal with caustic soda (formed by the action of the lime on the sodium carbonate), calcium sulphide, and sodium carbonate.

(γ.) The black ash is now treated with water to dissolve out the sodium carbonate. The clear solution is poured off and evaporated to dryness. The solid residue, consisting of more or less pure sodium carbonate, constitutes what is known as "*soda ash*."

Impurities of Soda Ash.—Sodium chloride, sodium sulphate, and sodium hydrate.

Purification of the Soda Ash.—The soda ash is first mixed with sawdust, and heated, whereby any sodium hydrate present is converted into sodium carbonate by the action of the carbonic anhydride evolved during the burning of the carbonaceous matter. The mass is then treated with water, and the filtered solution evaporated down and crystallized.

Very often, however, the clear solution of the "black ash" is at once concentrated by heat until the Na_2CO_3 is deposited, the mother liquor, known as "*red liquor*," being used in the preparation of sodium hydrate (*see* page 354).

Waste Products.—Hydrochloric acid is set free in the formation of the salt cake. If this were allowed to escape it would prove a nuisance. Hence in alkali works, it is usually absorbed by means of a wet coke scrubber. The liquid hydrochloric acid of commerce, largely used in the manufacture of bleaching-powder, etc., is commonly prepared in this manner.

Soda or Alkali Waste.—It may be noted that nearly all the sulphur of the sulphuric acid used, forms the insoluble calcium sulphide of the black ash, which, together with the excess of coal and lime, after its thorough exhaustion with water, forms the "soda," "alkali," or "tank waste." A part of this is now used in the preparation of sodium thiosulphate (hyposulphite) (*see* page 318), whilst the sulphur of the remaining portion is recovered by blowing air through the moist material in such quantity that a calcium persulphide and thiosulphate may be formed (Mond's Process). From this yellow liquor the sulphur is thrown down by the addition of hydrochloric acid:—

$$\begin{array}{ccccccccc} (1.)\ 12CaS & + & 6O_2 & = & 2CaS_5 & + & CaS_2O_3 & + & 9CaO. \\ \text{Calcic sulphide} & + & \text{Oxygen} & = & \text{Calcic persulphide} & + & \text{Calcic thiosulphate} & + & \text{Calcic oxide.} \end{array}$$

$$\begin{array}{ccccccccccc} (2.)\ 2CaS_5 & + & CaS_2O_3 & + & 6HCl & = & 3CaCl_2 & + & 3H_2O & + & 6S_2. \\ \text{Calcic persulphate} & + & \text{Calcic thiosulphate} & + & \text{Hydrochloric acid} & = & \text{Calcic chloride} & + & \text{Water} & + & \text{Sulphur.} \end{array}$$

Another process adopted for the recovery of the sulphur consists in adding to the soda-waste the liquor from chlorine stills (containing $MnCl_2$ and Fe_2Cl_6), whereby calcium chloride and the sulphides of iron and manganese are formed. These latter, on exposure to the air, become converted into oxides with the consequent separation of the sulphur:—

$$\begin{array}{ccccccccc} (1.)\ \underbrace{MnCl_2+Fe_2Cl_6}_{\text{Chlorine-still liquor}} & + & 4CaS & = & MnS & + & Fe_2S_3 & + & 4CaCl_2. \\ & + & \text{Calcic sulphide} & = & \text{Manganese sulphide} & + & \text{Iron sulphide} & + & \text{Calcic chloride.} \end{array}$$

$$\begin{array}{cccccccccccccc} (2.)\ 2MnS & + & O_3 & = & Mn_2O_3 & + & S_2; & 2Fe_2S_3 & + & 2O_3 & = & 2Fe_2O_3 & + & 3S_2. \\ \text{Manganese sulphide} & + & \text{Oxygen} & = & \text{Manganese oxide} & + & \text{Sulphur;} & \text{Iron sulphide} & + & \text{Oxygen} & = & \text{Iron oxide} & + & \text{Sulphur.} \end{array}$$

(3.) *Ammonia Soda Process.*—The details of this process are as follows:—

(*a.*) A concentrated solution of common salt is treated with ammonium hydric carbonate, hydric sodium carbonate and ammonium chloride being formed ($NH_4, HCO_3+NaCl = NaHCO_3+NH_4Cl$).

[In practice ammonia and CO_2 are passed into a solution of common salt ($NaCl+NH_3+H_2O+CO_2=NaHCO_3+NH_4Cl$).]

(*β.*) The sparingly soluble $NaHCO_3$ is now separated by crystallisation from the NH_4Cl.

(*γ.*) The hydric sodium carbonate is now heated until the normal sodium carbonate is formed ($2NaHCO_3 = Na_2CO_3+CO_2+H_2O$).

[The CO_2 evolved by this reaction is utilized to reconvert the ammonia compound from NH_4Cl into NH_4HCO_3.]

(4.) Sodium carbonate may also be obtained from cryolite ($3NaF, AlF_3$) by the action of heat on a mixture of cryolite and calcium carbonate ($2[(NaF)_3AlF_3]+6CaCO_3 = 2Al_2O_3,3Na_2O+6CaF_2+6CO_2$), the sodium aluminate being dissolved out and CO_2 passed through the remaining solution ($Al_2O_3,3Na_2O+3CO_2=3Na_2CO_3+Al_2O_3$).

Properties.—Sodium carbonate forms efflorescent crystals ($Na_2CO_3, 10H_2O$), which on exposure to air become white and opaque, losing one half of their water at 55° F. The crystals melt in their water of crystallization when heated to 122° F. (50° C.), ultimately leaving the anhydrous salt, Na_2CO_3. At a red heat, 1497·2° F. (814° C.), the anhydrous salt melts without decomposing. It has an alkaline taste and reaction, and is very soluble in water. (The crystals dissolve in the proportion of 1 in 2 parts of water at 60° F, and 1 in 1 at 212° F. The anhydrous salt dissolves in the proportion of 1 in 8 of water at 50° F.) Specific gravity of anhydrous salt, 2·46.

(N.B. Sodium carbonate is an *efflorescent* salt, whilst potassium carbonate is a *deliquescent* salt.)

(25.) Sodium Hydric Carbonate; *Bicarbonate of soda* ($NaHCO_3$).

Natural History.—Occurs naturally in many waters.

Preparation.—By exposing the moist crystals of the normal salt (Na_2CO_3) to the action of carbonic anhydride, or by saturating a solution of the salt with the gas. Considerable heat is evolved during the process, which is utilized in its manufacture. The salt also occurs in the course of the ammonia soda process (*q.v.*, p. 359).

Properties.—Bicarbonate of soda is less soluble than the normal salt (1 in 10 aq. at 50° F.). Thus its separation from the normal salt may be effected. Its solution in water is slightly alkaline. In preparing the salt from the carbonate, the so-called *sodium sesquicarbonate* (Na_2CO_3, $2(NaHCO_3)2H_2O$) is first formed, and afterwards a bicarbonate. Similarly by heating the dry salt or a solution of the bicarbonate, a sesquicarbonate is first formed (1), and then a carbonate (2):—

(1.) $4NaHCO_3 = Na_2CO_3,(2NaHCO_3) + H_2CO_3$.
(2.) $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$.

The carbonate of soda used in medicine is a bicarbonate, *i.e.*, a hydric sodium carbonate ($NaHCO_3$). It is not so soluble as the carbonate, and exhibits a very slightly alkaline reaction to turmeric, whereas the carbonate is very alkaline.

(26.) Sodium Potassic Carbonate ($NaKCO_3$). The anhydrous salt fuses more readily than either sodium or potassium carbonates. Hence it is employed to decompose the silicates by fusion.

(28.) Sodium Nitrate; *Cubic Nitre; Chili saltpetre* ($NaNO_3$). Found native in Chili and Peru. It crystallizes in rhombohedra, the crystals being deliquescent, on which account it cannot be used for gunpowder. It is very soluble in water (1 to 1). It fuses at 591° F. (310·5° C.) and is decomposed at higher temperatures. Specific gravity 2·1. It is used in the manufacture of nitric and sulphuric acids, and also in the preparation of potassium nitrate for gunpowder ("converted nitre") (*see* page 348). It is further employed as a dressing for soils.

(29.) Sodium Nitrite ($NaNO_2$) [*See* Potassium Nitrite, p. 350].

(30.) Sodium Chlorate ($NaClO_3$) [*See* Potassium Chlorate. $NaClO_3$ cannot, however, be separated from sodium chloride like

$KClO_3$ can from potassium chloride, because of the greater solubility of sodium chlorate over potassium chlorate (1 to 1).]

(31 to 34.) **Sodium Perchlorate, Bromate, Iodate, Periodate.** [*See* the corresponding Potassium Salts, p. 351.]

(42.) **Sodium Borate;** *Borax* ($Na_2O,2B_2O_3,10H_2O = 202 + 180 = 382$).

Preparation.—Crude borax (tincal), a compound of soda and boracic acid, was originally imported from Thibet, where it occurs as a natural production in the residue obtained from the evaporation of the water of certain lakes (page 219). It is usually prepared at the present time by fusing sodium carbonate with boric acid, or by mixing together their boiling solutions, the boric acid expelling carbonic anhydride from the sodium carbonate. The residue, if prepared by fusion, has to be dissolved out and crystallized.

Properties.—Specific gravity, 1·7. It forms hard, clear, prismatic efflorescent crystals, the transparency of which is soon destroyed by exposure to air. The solution (1 part of the salt in 40 of water at 32° F., and 2 parts in 1 of water at 212° F.), is alkaline. The crystals intumesce (swell up) at 167·9° F. (75·5° C.), and afterwards fuse to a colorless liquid, which, on cooling, presents the appearance of a glassy mass (vitrified borax). Fused borax [which melts at 1041·8° F. (561° C.)] possesses the power of dissolving many metallic oxides. Hence its use as a reagent in blowpipe analysis, the oxides imparting special colors to the borax bead by which they may be recognized. It is also used, for a similar reason, to remove any traces of oxide (or tarnish) from the surface of metals before soldering. It is employed as a flux; in enamelling (to render the enamels more fusible); in fixing colors on porcelain; in glazing stoneware; in medicine, etc.

Sodium Phosphates (see page 329).

(18.) **Sodium Phosphate** ($Na_3PO_4,12H_2O$).

Preparation.—(1.) By evaporating down a solution of Na_2HPO_4 in caustic soda.

(2.) By fusing 2 molecules of Na_2HPO_4 with 1 molecule of Na_2CO_3, dissolving the mass in water, and crystallizing.

Properties.—A soluble, efflorescent salt. Its solution exposed to air absorbs CO_2, forming Na_2CO_3 and HNa_2PO_4.

(19.) **Sodium Hydric Phosphate.**—*Phosphate of soda* ($Na_2HPO_4, 12H_2O = 142 + 216 + 358$).

Preparation.—By adding sodium carbonate or hydrate to the calcium phosphate obtained during the process of preparing phosphorus:—

$$\underset{\text{Calcic phosphate}}{H_4Ca2PO_4} + \underset{\text{Sodium carbonate}}{2Na_2CO_3} = \underset{\text{Calcic carbonate}}{CaCO_3} + \underset{\text{Water}}{H_2O} + \underset{\text{Carbonic anhydride}}{CO_2} + \underset{\text{Sodium hydric phosphate.}}{Na_2HPO_4.}$$

Properties.—The crystals are rhombic, efflorescent, and soluble in cold water (1 in 4). Sp. gr. 1·52. Solution alkaline.

Action of heat.—When heated to 99° F. (37·2° C.), the crystals melt in their own water of crystallization. Heated to 212° F. (100° C.), they lose their 12 molecules of water, becoming Na_2HPO_4. Heated to redness two molecules of the salt lose one more molecule of water, *sodium pyrophosphate* ($Na_4P_2O_7$) being formed. If free phosphoric acid (H_3PO_4) be added to this salt ($Na_4P_2O_7$), the *biphosphate of soda* or *sodic dihydric phosphate* is formed (NaH_2PO_4,H_2O). Phosphate of soda has an acid reaction.

Sodium hydric phosphate was formerly used in calico printing under the name of "dung substitute," sodium arsenate being now more generally used in its place.

The *tribasic* phosphates of soda (and the biphosphate of soda) give *yellow* precipitates with argentic nitrate.

(21.) Sodium Pyrophosphate ($Na_4P_2O_7,10H_2O$) (*see* above) crystallises in prisms. Its solution is alkaline. Boiled with an acid it becomes H_2NaPO_4.

The *tetrabasic* pyrophosphate gives a *white* precipitate with argentic nitrate, remaining unchanged by exposure to light.

(22.) Sodium Metaphosphate ($NaPO_3$).

Preparation.—By heating either the sodium dihydric phosphate (NaH_2PO_4) or microcosmic salt to redness.

Properties.—A non-crystalline, deliquescent, soluble substance (1 in 10 aq., and 1 in 1 at 100° F.), the solution having a feebly acid reaction.

The *monobasic* phosphate gives a *white gelatinous* precipitate with argentic nitrate.

(39.) Silicates of Sodium.

Silica or silicic acid has the power at a high temperature of expelling carbonic anhydride from its compounds. Hence various silicates may be formed by fusing silica with sodium carbonate.

The salt $Na_2O,SiO_2,9H_2O$ (Futsche) may be prepared by fusing 2 parts of powdered flint with 3 parts of sodium carbonate.

The salt $Na_2O,36SiO_2$ (Forchhammer) may be prepared by boiling finely divided silica in a saturated solution of sodium carbonate.

There are, moreover, many other silicates. The silicate $Na_2O,4SiO_2$ or "*soluble glass*" is prepared by fusing 15 parts of sand with 8 parts of sodium carbonate and 1 part of charcoal (Fuchs). The silica expels the CO_2, its liberation being assisted by the carbon which converts it into carbonic oxide. The mass is insoluble in cold, but soluble in boiling water (1 in 5 aq.). The solution is alkaline.

It is used for stone preservation, in fresco-painting (Stereochromy), as a dung substitute in calico-printing, etc.

Glass.

Glass is a compound of an alkaline silicate with a silicate of an alkaline earth and one or other of the metallic oxides, *i.e.*, a double silicate of potash (or soda) with lead (or lime, etc.). The following table represents the percentage composition of different glasses :—

	Window.	Plate.	Crown for optical purposes.	English flint.
Silica	66·37	73·5	62·5	51·93
Potash..	..	5·5	22·5	13·77
Soda	14·23	12·0	..	..
Lime	11·86	5·5	12·5	..
Alumina	8·16	3·5	2·5	0·47
Oxide of lead..	..	..	..	33·28
Oxide of iron and manganese ..	..	..	..	0·25

Soda always imparts a slight tinge of green to glass, which does not occur when potash is used. A soda glass, however, is more fusible and more brilliant than a potash glass.

Lime diminishes the fusibility of glass, imparts no color, and increases hardness and lustre. If an excess of lime be used, however, the glass on cooling turns milky.

Lead increases the fusibility and the lustre of the glass, and renders it softer.

Baryta is also said to increase its fusibility.

Window glass consists of the silicates of soda, lime and alumina. 100 parts of sand, 35 to 40 of chalk, 30 to 35 of soda ash, and 50 to 150 of "*cullet*" or broken glass, are first subjected to a low heat, so as to expel any moisture present, and to drive off a certain quantity of carbonic acid by which subsequent frothing is prevented. The heat is then sufficiently raised to effect the complete fusion of the materials. Sometimes sodium sulphate is used instead of sodium carbonate (soda ash), the sulphuric anhydride being expelled by the silica, as SO_3. Sometimes a little charcoal is added, whereby the SO_3 is reduced to SO_2, its expulsion being thus effected at a lower temperature. After melting, the mixture is allowed to remain for the "glass gall," or "sandiver," or "scum" (Na_2SO_4 and NaCl) to collect, which is then skimmed off.

Plate-glass consists of the silicates of soda, lime and potash ; 300 parts of pure white sand, 100 of sodic carbonate, 43 of slaked lime, and 300 of glass fragments being the proportions of the several constituents commonly employed in its manufacture.

Crown-glass, for optical purposes, contains no soda, in order to avoid the green tint that the alkali imparts to the glass. Sometimes a little boric acid is used in the place of a portion of the silica.

Wine-bottle and *carboy glass* consists of the alkaline silicates and the silicates of lime and alumina, with oxide of iron. The constituents are 100 parts of common red (ferruginous) sand, 80 of soap-maker's waste, 80 of gas lime, 5 of clay, and 3 of rock salt.

Flint-glass (crystal).—The constituents of flint-glass are 300 parts of pure white sand, 200 of minium (red oxide of lead), 100 of refined pearlash, and 30 of nitre. The nitre is added in order to prevent the reduction of the lead, by oxidizing any matters that might otherwise effect it. The fusion of the materials is, for the same reason, carried on in a closed pot. No soda is used because of the tint it imparts to the glass, whilst lead is added in order to increase fusibility and its refractive and dispersive power. Crystal is easily scratched, and is disposed to tarnish and to change colour.

Bohemian glass consists chiefly of potassium and calcium silicates.

Devitrification.—Reaumur's porcelain glass is prepared by heating certain kinds of glass, such as bottle-glass, or the soluble soda-glass of Fuchs, to very nearly its melting point, and then slowly cooling, whereby it is changed into a hard, opaque, porcelain-like mass (devitrification), a change due to the separation and crystallization of the silicates. Its original transparent state may be restored by fusion. Such glass is less fusible than common glass, and is a fair conductor of electricity.

Enamelling is effected by diffusing certain white opaque substances, such as stannic or antimonious oxides, through the glass.

Colouring.—This is effected by dissolving certain metallic oxides in the glass. The glass generally used for this purpose contains a little borax and about 53 per cent. of oxide of lead (paste or strass). Ferrous oxide imparts a *green* color; oxides of silver and antimony, a *yellow;* finely-divided charcoal, a *brownish yellow;* uranic oxide, a *greenish opalescent yellow;* cupric oxide (CuO) or chromic oxide, an *emerald green;* cuprous oxide (Cu_2O), a *ruby-red;* gold and stannic oxide, a more brilliant *ruby-red;* manganese peroxide a *violet;* oxide of cobalt, a *blue;* oxides of cobalt and manganese, a *black.*

It will be remarked that whilst ferrous oxide imparts a green color to glass, ferric oxide imparts no color. Hence a little nitre or arsenious acid, or Pb_3O_4, is often added to the glass, in order to oxidise any ferrous oxide that may be present. Similarly, the black oxide of manganese is sometimes used, which converts the ferrous oxide into ferric oxide, the manganese oxide becoming a protoxide, which, like ferric oxide, also imparts no color to the glass.

Painting on glass is effected by painting on a somewhat non-fusible glass with a finely-powdered and very fusible glass mixed with turpentine and the oxide requisite to impart the color desired. A sufficient heat is then applied to melt the fusible glass paint.

Colored glass is generally flashed, that is, colored only on the surface by dipping the uncolored glass into the colored glass pot.

REACTIONS OF SODIUM COMPOUNDS.

Sodium salts are all white if the acid be colorless. They are easily fusible and volatile at high temperatures.

(1.) Flame reaction—monochromatic (yellow).

(2.) Spectrum. Two bright lines coincident with the D lines of the solar spectrum.

(3.) *Potassium Metantimonate.* White crystalline precipitate of dihydric disodic pyrantimonate ($H_2Na_2Sb_2O_7,6H_2O$).

LITHIUM (Li_2).

Atomic weight = 7. *Monad* (LiCl). *Specific gravity*, 0·593. *Specific heat*, 0·9408. *Fuses at* 356° F. (180° C.).

History.—(λιθος, a stone.) Lithia was discovered by Arfvedson (1817). The metal was first prepared in small quantities by Davy, and in bulk by Matthiessen (1855).

Natural History.—It is a widely, but sparingly distributed-metal. It is found in all three kingdoms of nature. In the (α) *animal*, it occurs in milk and in blood; in the (β) *vegetable*, in tobacco; in the (γ) *mineral*, in all waters, also in lepidolite, petalite, triphane (spodumene), triphylline, etc.

Preparation.—By the electrolysis of fused lithium chloride, hard gas coke being used for the positive, and an iron wire for the negative pole.

Properties.—(α.) *Physical.* Lithium is a soft, white substance, and is the lightest metal known. Sp. gr. 0·593. It is very ductile and volatile, and burns with a brilliant *crimson* flame. It can be welded.

(β.) *Chemical.* Its reactions are similar to those of sodium and potassium, but it is less readily oxidised. Like potassium, lithium decomposes water at ordinary temperatures, but it does not inflame.

Uses.—Its salts are used in gout as a solvent for uric acid.

SALTS OF LITHIUM.

The Lithium compounds are analogous to the sodium and potassium salts. The best known are the following:—

Lithium oxide (*Lithia*) (Li_2O); *lithium hydrate* (LiHO) a body which rapidly corrodes platinum; *lithium chloride* (LiCl); *lithium iodide* ($LiI,3H_2O$); *lithium fluoride* (LiF); *lithium sulphate* (Li_2SO_4,H_2O), a crystalline soluble salt; *lithium nitrate* ($LiNO_3$); *lithium perchlorate* ($LiClO_4$); *lithium phosphate* (Li_3PO_4), a salt soluble in dilute acids, but insoluble in alkaline solutions or in solutions of alkaline phosphates; and *lithium carbonate* (Li_2CO_3), a very sparingly soluble salt.

Reactions of Lithium Compounds.

(1.) The salts commonly are fusible and deliquescent.

(2.) They communicate a red color to the blowpipe flame.

(3.) They give a non-continuous spectrum, showing a crimson band between B and C, and a faint band in the orange.

(4.) They corrode platinum foil when heated upon it.

(5.) *Potassium carbonate* gives a white precipitate of lithium carbonate in cold and very concentrated solutions.

(6.) *Hydric disodium phosphate* gives a white precipitate in a neutral or alkaline solution, soluble in acids and in ammonium salts.

CÆSIUM (Cs_2).

Atomic weight, 133. *Monad* (CsCl). *Specific gravity*, 1·88.

History.—(*Cæsius*, blue.)—Discovered by Bunsen and Kirchhoff (1860), in the Dürkheim water.

Natural History.—Found in certain minerals (*pollux*, a rare silicate), and in some waters.

Preparation.—By the electrolysis of a mixture of fused cæsium and barium cyanides. (The $BaCy_2$ is added to increase fusibility.)

(The metal cannot be prepared, like Rubidium, by the action of carbon on a cæsium carbonate.)

Properties.—A white, soft metal. Specific gravity 1·88. Fuses at 80·6° F. (27·0° C.). Inflames spontaneously in air or on water. It is the most electro-positive of all the metals. In its general properties it is very like potassium. Its spectrum consists of two bright blue lines almost coincident with the strontium blue line Srδ.

The compounds of cæsium best known are as follows :—

Cæsium oxide (cæsia, Cs_2O) ; *cæsium hydrate* (CsHO) ; *cæsium chloride* (CsCl), a body that forms double salts with other metallic chlorides ; *cæsium sulphate* (Cs_2SO_4), a body forming double salts with sulphates of the class to which magnesium sulphate belongs ; *hydric cæsium sulphate* ($CsHSO_4$) ; *cæsium nitrate* ($CsNO_3$) ; *cæsium carbonates* (Cs_2CO_3 and $HCsCO_3$).

The *cæsium platinic chloride* is far less soluble in water than the potassium platinic chloride.

RUBIDIUM (Rb_2).

Atomic weight, 85·3. *Monad* (RbCl).

History.—(*Rubidus*, dark red.)—Discovered by Bunsen and Kirchhoff (1860).

Natural History.—Widely distributed in minute quantities. It is found in the ashes of plants, in Lepidolite, in certain mineral springs, as *e.g.*, in a spring at Dürkheim, from which it was first obtained.

Preparation.—(1.) By the electrolysis of the fused chloride.

(2.) By heating together carbon and rubidium carbonate.

Properties.—A yellowish-tinted soft metal. Sp. gr. 1·52. Fuses at 101·3° F. (38·5° C.). Boils at a red heat, giving off a greenish vapor. Inflames when exposed to the air, but is less readily oxidised than cæsium. Burns when thrown into water, or when brought into contact with the haloid elements. It combines also with sulphur and arsenic.

Spectrum.—Two violet lines between Srδ and the blue potassium line, and two red lines beyond Frauenhofer's line A.

COMPOUNDS OF RUBIDIUM.

Rubidium chloride ($RbCl$), which forms double chlorides (*e.g.*, $PtCl_4$ $2RbCl$); *rubidium bromide* and *iodide* ($RbBr$ and RbI); *rubidium hydrate* ($RbHO$); *rubidium nitrate* ($RbNO_3$); *rubidium chlorate* ($RbClO_3$), and *perchlorate* ($RbClO_4$); *rubidium carbonates* (Rb_2CO_3,H_2O and $HRbCO_3$); *rubidium sulphates* (Rb_2SO_4 and $RbHSO_4$); *rubidium dithionate* ($Rb_2S_2O_6$); *rubidium borate* ($Rb_2O,2B_2O_3,6H_2O$).

NOTE.—*Cæsium carbonate* is soluble in absolute alcohol. *Rubidium carbonate* is nearly insoluble. The rubidium salts are isomorphous with those of potassium and cæsium.

AMMONIUM (NH_4 or Am′).

Ammonium (Am′) is a hypothetical metal, of which a supposed amalgam has been prepared. (*See* page 262.)

Preparation.—(1.) By electrolysing ammonium chloride, a globule of mercury being employed for the negative terminal.

(2.) By placing potassium amalgam in a warm solution of ammonium chloride.

In these cases the mercury swells enormously, owing, it is believed, to the formation of an amalgam of the metal NH_4. The bulk of the ammonium amalgam varies with the pressure very much like a gas, on account of which many consider that the so-called amalgam is simply mercury swollen by ammonia and hydrogen. The ammonium amalgam, however, rapidly decomposes into mercury, ammonia, and hydrogen, the last two gases being in the proportion of $2NH_3$ to H_2.

The ammonium theory depends largely on the circumstance that the combination of dry ammonia-gas (NH_3) with the anhydrides, such as CO_2 and SO_3, etc., forms a class called the *ammonides*, which present a very slight resemblance to the corresponding soda or potash salts. Thus *sulphuric ammonide* [$(NH_3)_2SO_3$] is a soluble crystalline body, but its solution is not precipitated by barium chloride as the true sulphates are, nor by platinum chloride as true ammonium salts are. By long boiling, however, the *sulphuric ammonide* [$(NH_3)_2SO_3$] becomes *ammonic sulphate* [$(NH_4)_2SO_4$], the change really consisting in the assimilation of one molecule of water by two ammonia molecules. In the case, however, of the hydracids, a true ammonium salt (as NH_4Cl) is formed independently of a water molecule, the hydrogen of the hydracid itself supplying the hydrogen atom required to form the ammonium radical.

Compounds of the Hypothetical Metal Ammonium ($NH_4=18$).

		Names.	Formula (general).	Molecular Weight.	Specific Gravity.
1		Ammonium hydrate (p. 368)	$(NH_4)HO$	35	
2	Haloids.	,, chloride (p. 368)	NH_4Cl	53·5	1·578
3		,, platinic-chloride	$2NH_4Cl,PtCl_4$		
4		,, iodide (p. 368)	NH_4I	145	
5		,, bromide (p. 368)	NH_4Br	98	
6		,, fluoride (p. 368)	NH_4F		
7		,, fluosilicate	$2NH_4F,SiF_4$		
8	Sulphides.	,, sulphide (p. 368)	$(NH_4)_2S$	68	
9		,, disulphide (p. 370)	$(NH_4)_2S_2$	100	
10		,, pentasulphide (p. 370)	$(NH_4)_2S_5$		
11		,, heptasulphide (p. 370)	$(NH_4)_2S_7$	260	
12		,, sulphhydrate (p. 370)	NH_4HS	51	
13	Sulphates, etc.	,, sulphate (p. 371)	$(NH_4)_2SO_4$	132	1·755
14		,, hydric sulphate (p. 371)	$(NH_4)HSO_4$	115	
15		,, sodic sulphate (p. 371)	$NH_4NaSO_4 2H_2O$		
16		,, pyrosulphite	$(NH_4)_2S_2O_5$		
17		,, dithionate	$(NH_4)_2S_2O_6,H_2O$		
18		,, thiosulphate	$(NH_4)_2S_2O_3,H_2O$		
19		,, sulphite	$(NH_4)_2SO_3,H_2O$		
20		,, chlorate	NH_4ClO_3		
21		,, perchlorate	NH_4ClO_4		
22		,, bromate	NH_4BrO_3		
23		,, iodate	NH_4IO_3		
24	Carbonates.	,, carbonate (normal), (p. 371)	$(NH_4)_2CO_3,H_2O$	96 + 18	
25		,, sesquicarbonate (p. 371)	$(NH_4)_2CO_3,2NH_4HCO_3$	254	
26		,, bicarbonate (p. 371)	NH_4HCO_3	78	1·58
27		,, nitrate (p. 371)	NH_4NO_3	80	1·635
28		,, nitrite (p. 372)	NH_4NO_2		
29	Phosphates.	,, phosphates (p. 372)	$(NH_4)_3PO_4.3H_2O$ $(NH_4)_2HPO_4$ $(NH_4)H_2PO_4$	= 132	1·64
30		,, pyrophosphate	$(NH_4)_4P_2O_7$		
31		,, sodic hydric phosphate (microcosmic salt) (p. 372)	$Na(NH_4)HPO_4,4H_2O$	137 + 72	1·6

(1.) **Ammonium Hydrate.**—*Ammonia* (NH_4HO or NH_3,H_2O or AmHO). The hydrate has not been isolated, but may be assumed to exist in the aqueous solution of ammonia gas. When the liquid is heated, ammonia and water are expelled. Hence, supposing the existence of a hydrate, the affinity must be of a very feeble nature. The oxide is not known.

HALOID SALTS.

(2.) Ammonium Chloride (NH_4Cl).—*Sal ammoniac.*

Natural History.—Found in the neighbourhood of volcanoes.

Preparation.—By the combination of ammonia and hydrochloric acid. In commerce it is prepared from gas liquor, which contains ammonia (derived from the nitrogen of coal) as a carbonate and sulphide, etc., or from the water distillate obtained from bones in the course of the preparation of animal charcoal. The ammoniacal liquor is either at once neutralised with HCl, and the salt crystallised out and purified by distillation, or the free ammonia, evolved by heating the liquor with lime, is conveyed directly into hydrochloric acid.

Properties.—The chloride is a white solid, without smell, crystallising in cubes and octahedra. It is slightly soluble in alcohol, but very soluble in water with great depression of temperature (1 in 3 at 60° F., and 1 in 1 at 212° F.). The saturated solution boils at 239° F. (115° C.). It is slightly acid to litmus. It is volatile at a moderate heat without fusing, undergoing *temporary* decomposition, when heated above a certain temperature, into hydrochloric acid and ammonia (*dissociation*). Hence the vapor density of this, as well as of several other ammonium salts, is abnormal. The relative weight of the vapor is 13·3, so that one molecule (53·5 parts) instead of occupying two volumes would seem to occupy four. Similarly, dissociation occurs when a neutral (but not an acid) solution of the salt is boiled, the steam carrying off the NH_3. Ammonium chloride forms double salts with various metallic chlorides (*e.g.*, $2NH_4Cl,PtCl_4$). This platinum compound is used for the quantitative determination of ammonium compounds, metallic platinum remaining in the crucible after the double chloride has been ignited.

Uses.—In soldering and tinning to produce clean metallic surfaces. It effects this by converting the oxides into fusible chlorides. It is also employed in dyeing and in medicine.

(4 to 6.) The **Ammonium Iodide** (NH_4I) and **Bromide** (NH_4Br) (prepared by the action of the haloid acids on ammonia) are used in photography. They are both soluble salts, the former decomposing rapidly on exposure on air. **Ammonium Fluoride** (NH_4F) is prepared in a similar manner.

THE SULPHIDES.

(8.) Ammonium Sulphide.—*Protosulphide* [$(NH_4)_2S$].

Preparation.—By the union of one volume of H_2S with two volumes of NH_3 at 0° F. (—18° C.)

Properties.—It consists of colorless crystals, very soluble in water.

It is a very unstable body, undergoing dissociation into ammonia and ammonium-hydric sulphide above 0° F. (—18° C.).

(12.) **Ammonium-hydric Sulphide.**—*Hydrosulphate of ammonia; Ammonium sulphhydrate* (NH_4HS).

Preparation.—(1.) (*As a solution.*) By saturating a solution of ammonia with sulphuretted hydrogen.

(2.) (*Anhydrous.*) By the admixture of equal volumes of ammonia and sulphuretted hydrogen.

(3.) By passing H_2S into alcoholic ammonia.

Properties.—The anhydrous salt is colorless, transparent, very volatile, subliming unchanged, or undergoing dissociation into NH_3 and H_2S, which reunite on cooling. Soluble in water.

The solution (the usual laboratory reagent) is at first colorless, but speedily becomes yellow by absorbing oxygen, whereby ammonium disulphide and thiosulphate are formed :—

$$8NH_4HS + 5O_2 = 2[(NH_4)_2S_2] + 2[(NH_4)_2S_2O_3] + 4H_2O.$$

Finally sulphur is deposited, the solution then containing thiosulphate, sulphite and sulphate of ammonium.

The solution of NH_4HS is largely used in the laboratory as a test reagent. Two important facts should be remembered :—

(1.) On the addition of *an acid*,—(*α.*) *the fresh solution* gives off H_2S, the solution itself remaining *clear* :—

$$NH_4HS + HCl = NH_4Cl + H_2S\ ;$$

(*β.*) *Whilst the old solution*, which also gives off H_2S, becomes *turbid* from the deposition of sulphur by the action of the acid on the ammonium disulphide :—

$$(NH_4)_2S_2 + 2HCl = 2NH_4Cl + H_2S + S.$$

(2.) On the addition of *acetate of lead*, (*α.*) *the fresh solution* gives a *black* precipitate of plumbic sulphide (PbS) ;

(*β.*) Whilst the *old solution* gives a *red* precipitate, due probably to the formation of a persulphide.

Boyle's fuming liquor (prepared by distilling sal-ammoniac with lime and sulphur) is the *hydrated diammonium sulphide.* Its solution in water, which dissolves sulphur freely, forms an **Ammonium Pentasulphide** [$(H_4N)_2S_5$], from which solution the sulphur may be obtained in oblique rhombic prisms. An **Ammonium Heptasulphide,** with the formula [$(H_4N)_2S_7$], has been obtained. It is a red crystalline body.

AMMONIUM OXY-SALTS.

(13.) **Ammonium Sulphate** [$(NH_4)_2SO_4$].—*Preparation.* By distilling gas liquor either alone or with lime, and condensing the ammonia set free in sulphuric acid. It is found native as mascagnite.

Properties.—A crystalline salt (six-sided rhombs), soluble in water (1 in 2 aq. at 60° F., and 1 in 1 at 212° F.) (Sp. gr. 1·75). When heated the crystals first decrepitate, then melt (284° F. or 140° C.), and finally decompose (500° F. or 260° C.), H_2O, NH_3, N, and SO_2 being formed.

It is used as a manure, and also to render muslin non-inflammable.

(14 and 15.) An acid or **Hydric Ammonium Sulphate** $(NH_4)HSO_4$ and a **Sodic Ammonium Sulphate** $(NH_4)NaSO_4,2HO$ are also known.

(24.) **Ammonium Carbonate (Normal)** $[(NH_4)_2CO_3,H_2O]$, is an unstable salt, prepared by saturating a solution of the sesquicarbonate with ammonia gas. Exposed to the air, it rapidly becomes (NH_4HCO_3). It dissociates at 136·4° F. (58° C.), CO_2,NH_3 and H_2O being formed.

(25.) **Ammonium Sesquicarbonate** (*common carbonate of ammonia, or Preston smelling salts*) $[(NH_4)_2CO_3,2(NH_4,HCO_3)=(NH_4)_4H_2(CO_3)_3]$ is prepared by heating chalk with ammonium chloride (or sulphate). The sesquicarbonate sublimes, and may be collected in a leaden vessel, and afterwards purified by sublimation :—

$$\underset{\text{Ammonium chloride}}{6NH_4Cl} + \underset{\text{Calcium carbonate}}{3CaCO_3} = \underset{\text{Calcium chloride}}{3CaCl_2} + \underset{\text{Ammonia}}{2NH_3} + \underset{\text{Water}}{H_2O} + \underset{\text{Ammonium sesquicarbonate.}}{[(NH_4)_4H_2(CO_3)_3]}$$

The salt smells strongly of ammonia, and is soluble in cold water (1 in 3 aq.).

On exposure to air the transparent sesquicarbonate gives off NH_3 and CO_2, the salt becoming opaque and crumbly, an *ammonium bicarbonate* being formed.

(26.) **Hydric Ammonium Carbonate** $(NH_4)HCO_3 = 78$ (*bicarbonate*) (Sp. gr. 1·58), is prepared by saturating a solution of ammonia with carbonic anhydride, or by the action of air or of a small quantity of water or alcohol on the sesquicarbonate. The water dissolves the normal carbonate and leaves the bicarbonate, it being the more sparingly soluble salt (1 in 8 aq.). A solution of the salt gives off CO_2, becoming ammoniacal even at ordinary temperatures.

(27.) **Ammonium Nitrate** (NH_4NO_3) is prepared by neutralising ammonium carbonate with nitric acid. It is a crystalline, deliquescent salt, losing ammonia as it deliquesces, and becoming acid. It is soluble in water with great absorption of heat. On the application of a temperature of 226° F. or 107·8° C. it melts, and at 482° F. or

250° C. undergoes decomposition into water and nitrous oxide, whilst at a still greater heat it is decomposed into water, nitric oxide and nitrogen. At low temperatures it absorbs ammonia.

(28.) Ammonium Nitrite (NH_4NO_2). *Preparation.*—(1) By the slow oxidation of phosphorus in moist air ; (2) by the action of ozone on dilute ammonia ; (3) by the combustion of hydrogen in air ; (4) by mixing ammonia, oxygen and nitric oxide in a dry flask ; or (5) by the action of barium nitrite on ammonium sulphate.

Properties.—A white crystalline body, decomposing at common temperatures into nitrogen and water, but exploding on the application of heat. It decomposes rapidly when dissolved.

(29.) Ammonium Phosphate ($(NH_4)_2HPO_4$) is prepared by saturating a solution of phosphoric acid with ammonium carbonate, and evaporating with the constant addition of ammonia. It is soluble in water, and is much used in the laboratory as a reagent.

(31.) Sodic Ammonic Hydric Phosphate, Microcosmic Salt (*μικρὸς*, little, and *κοσμός*, a world) ($Na,NH_4,H,PO_4,4H_2O$), is the only ammonium phosphate of importance, although phosphates corresponding to the sodium phosphates are known. It occurs in guano and in stale urine.

Preparation.—By mixing boiling solutions of 1 part of ammonium chloride and 6 parts of hydric sodium phosphate ($Na_2HPO_4 + NH_4Cl = NH_4NaHPO_4 + NaCl$). The microcosmic salt is purified by successive recrystallizations.

Properties.—It is very soluble, the solution having an alkaline reaction. On the application of heat, ammonia and water are driven off, a sodium metaphosphate remaining ($NH_4NaHPO_4 = NaPO_3 + NH_3 + H_2O$). This compound (like borax) becomes a colorless glass at a red heat, in which state it dissolves various metallic oxides, forming with them beads of different colors. Hence its use in blow-pipe experiments.

REACTIONS OF AMMONIUM COMPOUNDS.

Ammonium salts are white unless the acid be colored, and entirely volatile unless the acid be fixed, in which latter case only ammonia is evolved.

Flame.—No color is imparted to a flame by ammonium compounds.

Platinic chloride.—A ppt. of ($PtCl_4,2NH_4Cl$), which on ignition leaves metallic platinum only.

Tartaric Acid or *Acid Sodium Tartrate*, a white crystalline precipitate of $NH_4,HC_4H_4O_6$.

Heated with calcium hydrate or caustic soda or potash, ammonium compounds evolve ammonia, known by—(1) its smell; (2) its browning turmeric; (3) and its forming white fumes with HCl.

Nessler reagent (mercuric iodide dissolved in a solution of potassium iodide and caustic potash) gives either a brown discoloration or a precipitate, according to the quantity of ammonia present. [This reaction does not occur in the presence of alkaline sulphides or cyanides.]

CHAPTER XIV.

THE METALS OF THE ALKALINE EARTHS.

BARIUM and its Compounds — STRONTIUM and its Compounds — CALCIUM and its Compounds—MAGNESIUM and its Compounds.

Metal.	Symbol.	Atomic Weight.	Specific Gravity.	Electric Conductivity 68°—72° F.
Barium	Ba	137·0	4·0	..
Strontium	Sr	87·5	2·54	6·71
Calcium	Ca	40·0	1·57	22·14
Magnesium	Mg	24·0	1·74	25·47

We class magnesium with the metals of the alkaline earths for convenience, although its power of resisting oxidation at ordinary temperatures, its volatility at a high temperature, the sparing solubility of its oxide and sulphide, and the solubility of its sulphate, more nearly ally it to zinc and cadmium than to the metals of this group.

Barium, strontium and calcium are distinguished from the alkaline metals as follows :—

(1.) They are dyad elements, the alkaline metals being monads.

(2.) They are heavier than water, the alkaline metals being lighter.

(3.) They decompose water less energetically.

(4.) Their oxides and sulphides are less soluble in water.

(5.) Their carbonates are insoluble in pure water, but soluble in water containing CO_2.

(6.) Their sulphates, phosphates and oxalates are nearly insoluble.

(7.) They each form two oxides, of which one is basic, and forms a hydrate with water, having the formula $M''H_2O_2$.

(8.) They each form one chloride, of the formula $M''Cl_2$.

BARIUM ($Ba'' = 137$).

Atomic weight, 137. *Specific gravity*, 4·0. *Atomicity*, *dyad* ($Ba''Cl_2$).

History.—Isolated by Sir H. Davy (1808).

Natural History.—Does not occur native. It is chiefly found as *heavy spar* ($BaSO_4$) and as *Witherite* ($BaCO_3$). Traces of the metal in combination have been found in some few mineral waters.

Preparation.—(1.) By electrolysing fused or moistened barium chloride. In the latter case mercury is employed for the negative pole, an *amalgam of barium* resulting. The mercury is afterwards driven off by heat in a current of hydrogen.

(2.) An amalgam of barium may also be formed by the action of sodium amalgam on a solution of barium chloride.

(3.) By passing the vapor of potassium over red-hot barium oxide or chloride, and extracting the metal with mercury.

Properties.—A pale yellow, malleable metal. Melts below a red heat. Tarnishes in air. Decomposes water at ordinary temperatures ($Ba + 2H_2O = H_2 + BaH_2O_2$), and glass at a red heat. Sp. gr. 4·0.

Compounds of Barium ($Ba = 137$).

	COMPOUNDS.	Formula.	Molecular weight of anhydrous salt.	Specific gravity of crystals.	BaO in 100 parts.
1	Barium oxide (baryta). (p. 376) ..	$Ba''O$	153	4·73	100·00
2	,, dioxide (p. 376)	BaO_2	169		90·53
3	,, hydrate (p. 376)	BaH_2O_2	171	4·495	89·47
4	,, chloride (p. 376)	$BaCl_2, 2H_2O$	208+36	3·052	73·55
5	,, bromide ..	$BaBr_22H_2O$			
6	,, iodide	BaI_22H_2O			
7	,, fluoride	BaF_2			
8	,, fluosilicate ..	BaF_2SiF_4			
9	,, sulphides (p. 376) (*α.*)	BaS	169		90·53
	,, ,, (*β.*)	BaS_4H_2O			
10	,, disulphide ..	BaS_2	201		76·11
11	,, sulphhydrate..	BaH_2S_2			
12	,, sulphate (p. 377)	$BaSO_4$	233	4·59	65·66
13	,, pyrosulphate. .	BaS_2O_7			
14	,, sulphite	$BaSO_3$			
15	,, dithionate ..	$BaS_2O_62H_2O$			
16	,, thiosulphate ..	BaS_2O_3, H_2O			
17	,, nitrate (p. 377)	$Ba2NO_3$	261	3·284	58·62
18	,, nitrite	$Ba2NO_2H_2O$			
19	,, carbonate (p. 377) ..	$BaCO_3$	197	4·3	77·67
20	,, chlorate (p. 377)	$Ba2ClO_3, H_2O$	304+18	3·0	50·32
21	,, perchlorate ..	$Ba2ClO_44H_2O$			
22	,, phosphates ..	$Ba_32PO_4H_2O$ $BaHPO_4$ BaH_42PO_4			

COMPOUNDS OF BARIUM WITH OXYGEN, ETC.

Barium oxide	BaO.
Barium peroxide	BaO_2.
Barium hydrate	BaH_2O_2.

(1.) **Barium Oxide,** *Baryta* (BaO), is the product of the combustion of the metal in air, and constitutes the residue left on igniting barium nitrate, or a mixture of barium carbonate with carbon. It is a greyish substance, fusible in the oxyhydrogen flame. (Sp. gr. 4·73). It freely absorbs moisture and carbonic anhydride, and slakes with water, forming barium hydrate (BaH_2O_2).

(2.) **Barium Peroxide,** or *Dioxide* (BaO_2) is prepared by heating barium oxide either with potassium chlorate or in a current of oxygen or of air at about 752° F. (400° C.). It is used in the preparation of hydroxyl (p. 248), and as a source of oxygen (page 70). It is a white powder, insoluble in water. When very strongly heated it gives off oxygen, leaving BaO.

Treated with sulphuric acid it evolves oxygen. Heated in a stream of SO_2, $BaSO_4$ is formed.

(3.) **Barium Hydrate,** *Caustic baryta* (BaH_2O_2). *Preparation.* (1.) By the action of water on baryta (BaO). (2.) By boiling barium sulphide with cupric oxide ($BaS + CuO + H_2O = BaH_2O_2 + CuS$). (3.) *Manufacturing process.* By first heating powdered heavy spar with carbon (forming BaS), then passing carbonic anhydride and steam over the residue (forming $BaCO_3$), and finally subjecting the carbonate formed to the action of superheated steam ($BaCO_3 + H_2O = BaH_2O_2 + CO_2$).

Properties.—It rapidly absorbs CO_2. It is not decomposed by heat. It is soluble in water (1 in 20 at 60° F., and 1 in 3 at 212° F., *baryta water*), but is almost insoluble in alcohol. Heated in a current of air, water is driven off and BaO_2 formed. Barium hydrate was formerly used to separate the uncrystallizable from the crystallizable sugar. It forms with cane sugar an insoluble compound ($C_{12}H_{22}O_{11}BaO$) which, when suspended in water and subjected to a stream of CO_2, yields sugar (which is soluble in the water), and $BaCO_3$ which is insoluble. SrH_2O_2 has of late been substituted for BaH_2O_2 for a similar purpose in the refining of sugar.

(4.) **Barium Chloride** ($BaCl_2,2H_2O$) is prepared by dissolving $BaCO_3$ or BaS in HCl, or by heating the sulphate with coal, limestone, and calcium chloride. It crystallizes in flat prisms, which are soluble in pure water (1 in 2 of water at 60° F.), but are much less soluble if the water contains any free acid. Sp. gr. 3·05. It is almost insoluble in alcohol or in strong mineral acids.

(9.) **Barium Sulphide** (BaS).—Prepared by pouring H_2S over the heated oxide, or by heating the sulphate with carbon (Bolognian phosphorus). It is a white body, and absorbs water, oxygen and CO_2 when exposed to the air. To see its phosphorescence the newly-made and hot sulphide should be preserved in sealed tubes (luminous paint). With water it forms a mixture of the hydrate and sulphhydrate ($2BaS + 2H_2O = BaH_2O_2 + BaH_2S_2$).

BARIUM OXY-SALTS.

(12.) **Barium Sulphate** ($BaSO_4$) is found native as heavy spar. The powder has a Sp. gr. of 4·5. It is almost insoluble in water (1 in 400,000 by weight) or in acids, excepting in boiling sulphuric acid. It is used by artists as a paint (*permanent white*), and is employed as an adulterant of white lead. Heated with carbon, it (in common with all sulphates) becomes a sulphide.

(17.) **Barium Nitrate** ($Ba2NO_3$) is prepared by the action of dilute HNO_3 on $BaCO_3$. The crystals are octahedral. Sp. gr. 3·2. It is insoluble in alcohol or in concentrated nitric acid, but is soluble in water (1 in 8 at 60° F., and 1 in 3 at 212° F.). It melts at 1106.6 F (597° C.). and is decomposed at a red heat ($2BaN_2O_6 = 2BaO + 2N_2O_4 + O_2$). It is used for green fire in pyrotechny.

(19.) **Barium Carbonate,** *Witherite,* Sp. gr. 4·3 ($BaCO_3$), is prepared by the action of an alkaline carbonate on a barium salt. Artificially prepared, it is a dense white powder. It is *insoluble* in water containing saline matter, *almost insoluble* in pure water (1 in 14,000), but *soluble* in water containing CO_2 (1 in 600 parts). It fuses at a white heat, when it gives off CO_2, but decomposition is more easily effected if it be mixed with carbon. It is used as a rat poison.

(20.) **Barium Chlorate** ($Ba(ClO_3)_2,H_2O$) is prepared either by neutralizing chloric acid with carbonate of barium and evaporating, or by passing chlorine into a hot solution of barium hydrate. It is soluble in cold water (1 in 4 of water). By heat it evolves oxygen, leaving a residue of chloride.

REACTION OF BARIUM COMPOUNDS.

Spectrum.—Complex. The two bright lines in the green, are those most marked.

Flame.—Barium colors the non-luminous flame green.

Sulphuric Acid and Soluble Sulphates.—White ppt. ($BaSO_4$), insoluble in dilute acids.

Alkaline Carbonates. A white ppt. of $BaCO_3$.

Hydrofluosilicic Acid.—White crystalline ppt. (SiF_4,BaF_2).

Potassium Chromate (or *Dichromate*).—Yellow ppt., insoluble in acetic acid.

STRONTIUM (Sr''=87·5).

Atomic weight, 87·6 ; *Specific gravity,* 2.54 ; *Atomicity, dyad* ($Sr''Cl_2$).

History.—Isolated by Sir H. Davy in 1808.

Natural History.—Found as *strontianite* ($SrCO_3$) and as *celestine* ($SrSO_4$). Traces also occur in brine springs, etc.

Preparation.—By electrolysis of the fused chloride (see Barium, p. 375).

Properties.—A yellow, malleable metal. It oxidises spontaneously on exposure, burns in air with a crimson flame, and decomposes water at common temperatures with the evolution of hydrogen. It melts at a red heat. It is soluble in dilute, but not in concentrated, nitric acid.

Compounds of Strontium (Sr = 87·6).

	Names.	Formula.	Atomic Weight of Anhydrous Salt.	Specific Gravity of Crystals.	SrO in 100 parts.
1	Strontium oxide (strontia)	SrO	103·6	4·611	100·0
2	,, dioxide ..	SrO_2	119·6		86·62
3	,, hydrate ..	$SrH_2O_2,8H_2O$	121·6	1·396	85·19
4	,, chloride ..	$SrCl_2,3H_2O$	158·6	1·603	65·32
5	,, bromide ..	$SrBr_26H_2O$			
6	,, iodide.. ..	SrI_27H_2O			
7	,, fluoride ..	SrF_2			
8	,, fluosilicate. .	$SrF_2SiF_4,2H_2O$			
9	,, sulphate ..	$SrSO_4$	183·6	3·9	56·43
10	,, sulphite ..	$SrSO_3$			
11	,, dithionate ..	SrS_2O_6,H_2O			
12	,, thiosulphate.	$SrS_2O_3,5H_2O$			
13	,, nitrate ..	$Sr2NO_3$	211·6	2·305	
14	,, carbonate ..	$SrCO_3$	147·6	3·65	70·19
15	,, chlorate ..	$Sr2ClO_3$			
16	,, phosphate, (like Barium)				

(1.) **Strontium Oxide.**—*Strontia* (SrO). Corresponds in all respects to BaO (*see* page 376).

(2.) **Strontium Dioxide** (SrO_2).

Preparation.—By the action of hydroxyl on strontium hydrate ($SrH_2O_2 + H_2O_2 = SrO_2 + 2H_2O$). It cannot be prepared, like BaO_2, by heating SrO in air.

(9.) **Strontium Sulphate** ($SrSO_4$) occurs native as celestine. It is precipitated by sulphuric acid from solutions of strontium salts. It is but very slightly soluble in water (0·015 part in 100 of water at

60° F.). Fuses at a bright red heat. It may be known from the barium salt by its conversion into carbonate when digested with a cold solution of an alkaline carbonate.

(13.) **Strontium Nitrate** ($Sr2NO_3$) is a deliquescent salt used in the manufacture of red fire. It is insoluble in nitric acid, but soluble in water (1 in 2 at 50° F., and 1 in 1 at 212° F.).

(14.) **Strontium Carbonate** ($SrCO_3$) is prepared by adding a solution of an alkaline carbonate to one of strontium nitrate. It occurs in nature as *strontianite.* It is sparingly soluble in water (1 in 18,000), and evolves CO_2 at a red heat.

Tests for Strontium Compounds.

All the strontium salts are white provided the acid with which the metal is combined be colorless.

1. Strontium compounds color a non-luminous flame red.

2. In the spectrum several bright bands are seen in the red and orange, and a brilliant band in the blue.

Tests similar to barium compounds, excepting that—

3. *Hydrofluosilicic acid* gives no precipitate with strontium salts, the compound (SrF_2,SiF_4) being soluble in water.

4. *Alkaline carbonates,* a white precipitate ($SrCO_3$).

5. A solution of strontium sulphate precipitates $BaSO_4$ from a solution of a barium salt.

6. *Potassium Dichromate;* no ppt. (*See* Barium, p. 377).

CALCIUM ($Ca''=40$).

Atomic weight, 40; *Specific gravity,* 1·578; *Atomicity, dyad* ($CaCl_2$); *Specific heat,* 0·167.

History.—Isolated by Davy, 1808.

Natural History.—Found (*a.*) in the *mineral* kingdom, as a *carbonate* in marble, limestone, calcspar, etc. ($CaCO_3$); as a *sulphate* in gypsum, selenite, alabaster, etc. ($CaSO_4$); as a *fluoride* in fluorspar; as a *phosphate* in apatite, phosphorite, etc.; as *syngenite* ($CaK_2,2SO_4$); as *glauberite* ($CaNa_22SO_4$); as *osteolite* and *sombrerite* ($Ca_3P_2O_8$), etc. It occurs in all spring and river waters; in the sun and some of the fixed stars, etc.

(*β.*) In the *animal* kingdom it is found in bones as a phosphate, and in eggshells, oystershells, etc., as a carbonate.

(*γ.*) It is present in all *vegetables.*

Preparation.—(1.) By processes similar to those described for the preparation of barium and strontium (*see* page 375).

(2.) By igniting sodium with calcium iodide.

(3.) By heating an alloy of zinc and calcium (formed by fusing together zinc, sodium, and calcium chloride) so as to volatilize the zinc. (Caron.)

(4.) By electrolysing a fused mixture of calcium, strontium, and ammonium chlorides. (Mathiesson).

Properties.—A light yellow, very hard, malleable, ductile metal. Specific gravity 1·578. It melts at a red heat, tarnishes in moist air, and decomposes water with the evolution of hydrogen. It is rapidly acted on by dilute acids. Concentrated nitric acid has no action upon it, calcium in this respect resembling the passive state of iron. The heated metal burns with a brilliant yellow light.

Compounds of Calcium (Ca = 40).

	Names.	Formula.	Atomic Weight of Anhydrous Salt.	Specific Gravity of the Crystal.	Ca or CaO in 100 parts.
1	Calcium oxide (quick lime)	CaO	56	3·18	Ca=71·43
2	,, dioxide.. ..	CaO_2			
3	,, hydrate (slaked lime)	CaH_2O_2	74	2·078	CaO=75·68
4	,, chloride ..	$CaCl_2$	111	Crystallized 1·680 Fused .. 2·485	Ca=36·03
5	,, bromide ..	$CaBr_2$			
6	,, iodide	CaI_2			
7	,, fluoride (fluor spar)	CaF_2	78	3·4	Ca=51·28
8	,, fluosilicate ..	CaF_2,SiF_4			
9	,, sulphide ..	CaS	72		
10	,, disulphide ..	CaS_2			
11	,, pentasulphide	CaS_5			
12	,, phosphide ..	Ca_2P_2 (?)	142		
13	,, disilicide ..	$CaSi_2$			
14	,, carbonate (chalk) ..	$CaCO_3$	100	2·72	CaO=56·00
15	,, sulphate (gypsum)	$CaSO_4$	136	Crystallized 2·30 Anhydrous 2·95	CaO=41·18
16	,, potassic sulphate (syngenite) ..	CaK_22SO_4,H_2O			
17	,, sodic sulphate (glauberite)	$CaNa_22SO_4$			
18	,, thiosulphate. .	$CaS_2O_36H_2O$			
19	,, dithionate ..	$CaS_2O_64H_2O$			
20	,, sulphite ..	$CaSO_3,2H_2O$			
21	,, nitrate	$Ca2NO_3,4H_2O$	164	Crystallized 1·780 Anhydrous 2·24	
22	,, hypochlorite. .	$CaCl_2O_2$			
23	,, ortho-phosphates	$Ca_3P_2O_8$ (bone earth) $CaHPO_42H_2O$ $CaH_4(PO_4)_2H_2O$ (superphosphate)			
	pyro-	$Ca_2P_2O_7$			
	meta-	CaP_2O_6			
24	,, hypophosphite	$CaH_4P_2O_4$			
25	,, oxalate.. ..	$CaC_2O_4,2H_2O$	128		

Compounds of Calcium with Oxygen and Hydroxyl.

Calcium oxide	CaO.
Calcium peroxide	CaO_2.
Calcium hydrate	CaH_2O_2.

(1.) **Calcium Oxide;** *Lime; Quicklime* (CaO). *Preparation.*—(1.) By heating a mixture of coal with limestone or chalk ($CaCO_3$). "Lime" is prepared commercially by heating the mixture in properly constructed kilns, the mixed material being put in at the top of the furnace, and the quicklime taken out at the bottom. (2.) Pure CaO may be prepared by heating Carrara marble (*see* $CaCO_3$), or calcium nitrate to redness for some hours in a crucible.

Properties.—A white, caustic substance. Specific gravity 3·08. It combines rapidly with water (*slaking*), by which process great heat is evolved. The lime swells up during the process (*live-lime*), and finally crumbles to a white powder, forming CaH_2O_2, called *slaked lime* (*solid calcium hydrate*). If the limestone from which lime is prepared contains clay, it is apt to vitrify, whilst if the lime contains magnesia, it slakes badly (a poor lime). A lime that slakes well is called a rich lime. When exposed to the air it absorbs both moisture and carbonic anhydride, becoming what is called "*air-slaked*" lime, which is a mixture of $CaCO_3$ and CaH_2O_2.

CaO is used in the laboratory for drying gases. It is infusible, even in the oxyhydrogen blow-pipe, and is used therefore for the lime light.

(2.) **Calcium Peroxide** (CaO_2). Prepared like SrO_2 (*see* page 378).

(3.) **Calcium Hydrate,** *Slaked lime* (CaH_2O_2). Prepared by the action of water on CaO. Specific gravity 2·078. At a red heat it yields up H_2O, "quicklime" (CaO) being formed.

A white creamy mass called "*milk of lime*" is produced when calcium hydrate is diffused in water. Calcium hydrate is twice as soluble in cold (1 in 700 or 0·5 gr. to ℥j.) as it is in hot water, the solution being known as "*lime water*," an alkaline liquid, absorbing CO_2 from the air with avidity. By evaporating lime-water "in vacuo," a crystalline hydrate (CaH_2O_2) may be obtained (Gay Lussac).

Uses of Lime.

Mortar, *which is used for buildings exposed to the action of air only*, consists of lime and sand, the latter being added, as in the case of pottery, to increase cohesive power, and to prevent the mortar shrinking as it dries. Before the mortar is applied, the bricks are wetted, in order to prevent their absorbing moisture too rapidly from the mortar. It is not very clear why mortar "sets." The lime on the surface becomes a carbonate, whilst *possibly* a calcium silicate may be formed.

Mortar, when exposed to the action of water, disintegrates. Hence it cannot be used for sub-aqueous constructions.

Cements, or Hydraulic Mortars, *are employed for buildings exposed to the action of water.* They consist of a calcined mixture of carbonate of lime and clay (10 to 30 per cent.). [If too great a heat be applied in burning, the lime would be vitrified and would not slake, calcic and aluminic silicates being formed]. The powdered mass, when mixed with water, solidifies, owing to the formation of hydrated double silicates and aluminates. The material thus formed is of great hardness, and is not acted upon by water.

The rapidity of solidification depends on the quantity of clay present. If it contains 25 to 35 per cent., it hardens in a few hours, and constitutes what is called *Roman cement*, a substance commonly manufactured from the nodules of calcareo-argillaceous ironstone, found in the London clay.

Portland cement consists of a calcined mixture of lime with the clay of the Medway valley. The mass, when dry, has the appearance of Portland stone.

Concrete is a mixture of hydraulic cement with gravel or coarsely powdered pebbles. *Scott's cement* is lime containing a small proportion of calcium sulphate.

Lime is employed for many purposes, such as for manure, for the purification of coal gas, for the removal of hair from skins in tanning, for sugar refining, etc.

Haloid Salts.

(4.) **Calcium Chloride** ($CaCl_2$).—*Preparation.* (1.) By the action of HCl on $CaCO_3$. [To purify it from ferrous compounds, chlorine water is added in excess. Milk of lime is now added to render the solution alkaline. The precipitate formed after heating is filtered off (= ferric, manganic, and aluminic hydrates, etc.). Acidulate with HCl.] The solution is now evaporated to dryness, when $CaCl_2,6H_2O$ is obtained, which, at 390° F. becomes $CaCl_2,2H_2O$, and above this heat $CaCl_2$. (2.) It is obtained, as a by-product, in the manufacture of potassium chlorate and of ammonium carbonate (pages 35 and 371).

Properties.—A white, very deliquescent salt, soluble in absolute alcohol and in water (4 in 1 aq. at 60° F.), the saturated aqueous solution boiling at 355° F. (179·5° C.). Melts at 84·2° F. (29° C.) in its water of crystallization. Specific gravity of fused salt, 2·205. The fused salt absorbs water greedily. Boiled with CaH_2O_2, and filtered whilst the solution is hot, it deposits crystals of $Ca_2HClO_2,7H_2O$. It absorbs ammonia gas freely, forming ($CaCl_2,8NH_3$).

Uses.—It is used in the laboratory in the solid form as a desiccant.

Owing, however, to its absorptive power for ammonia, it cannot be used to dry this gas. Its solution is employed as a bath to obtain a steady, continuous temperature. A solution containing 50 per cent. of $CaCl_2$ boils at 233·6° F. (112° C.), a 325 per cent. solution boiling at 356° F. (180° C.). The crystals ($CaCl_2,6H_2O$) mixed with ice form a powerful freezing mixture [$-67°$ F. ($-55°$ C.)].

(7.) **Calcium Fluoride,** *Fluor spar* (CaF_2), is found as a mineral, having a variety of tints dependent on impurities. It also occurs in sea and other waters, in the bones and teeth of animals, etc. It is the source of all the fluorine compounds. It phosphoresces in the dark when heated. It is soluble in water (1 in 2000 aq. at 50° F.), and fuses at a red heat without decomposition. Used as a flux; for ornaments; etc.

(8.) The **Calcium Sulphides** are mostly soluble.

The monosulphide (CaS) may be prepared by reducing calcium sulphate with carbon. It is insoluble in water, but by prolonged boiling a sulphhydrate, CaS_2H_2, is formed. Certain higher sulphides (*e.g.*, CaS_4 and CaS_5) may be prepared by boiling sulphur in milk of lime.

Calcium monosulphide, which is that sulphide that has been most studied, forms one of the principal constituents of the "*soda waste*" of the alkali works. By exposure to air, it becomes calcium thiosulphate ($2CaS + H_2O + 2O_2 = CaH_2O_2 + CaS_2O_3$), which by the action of sodium carbonate is converted into sodium thiosulphate (*see* page 357). Calcium sulphide is luminous in the dark after exposure to a strongly actinic light (Canton's phosphorus; luminous paint).

OXY-SALTS OF CALCIUM.

(14.) **Calcium Sulphate** ($CaSO_4$) is found in nature as *anhydrite* ($CaSO_4$), *gypsum, alabaster, selenite,* etc. ($CaSO_4$, $2H_2O$). It also occurs in the soil and in various waters, constituting one source of *permanent hardness.*

Properties.—Occurs in flattened prisms (selenite) and in earthy masses (gypsum). It is soluble in water (1 in 500 (=140 grs. per gallon) at 60° F.), its solubility being diminished by the presence of calcium and magnesium chlorides in solution, but increased by the presence of dilute acids, ammoniacal salts, sodium chloride and thiosulphate. It is insoluble in alcohol and in dilute nitric and hydrochloric acids. It is soluble in concentrated sulphuric acid, the compound ($CaSO_4$, H_2SO_4) being formed, which on dilution with water, yields the normal salt and free acid. Boiled in a solution of an alkaline carbonate, it is decomposed, an alkaline sulphate and calcium carbonate being formed.

Uses.—*Plaster of Paris* or *burnt gypsum* consists of finely-powdered gypsum calcined at 392° F. (200° C.), so as to drive off its two molecules of water. When the calcined mass is mixed with water, it rapidly solidifies and *expands* (hence its value for making casts), recombining with the two molecules of water expelled by the previous heat. If "overburnt" (that is, heated above 200° C.) this property of recombination with water is destroyed. By exposure to air, plaster of Paris deteriorates, owing to its absorbing moisture. *Stucco* is plaster of Paris mixed with a solution of size, whilst various cements are formed by its admixture with a solution of alum, borax, etc., by which means the hardness of the mass, when set, is greatly increased. *Scagliola,* or *artificial marbles,* are formed by the insertion into the stucco of pieces of natural stone.

The "*pearl hardener*" of the paper-makers is freshly precipitated calcium sulphate.

(15.) **Calcium Nitrate** ($Ca2NO_3,4H_2O$) is a crystalline deliquescent salt, soluble in water and in alcohol. It is found as an efflorescence on moist walls, in nitre plantations, and wherever there is organic refuse, the calcium nitrate being formed from the oxidation of the ammonia in the presence of lime.

(16.) **Calcium Carbonate** ($CaCO_3$) may be prepared by precipitating a solution of a calcium salt with an alkaline carbonate, or by passing CO_2 (avoiding excess) into lime water. It is found native in an uncrystallized state as limestone, chalk, oolite, etc., and also in minute granular crystals (as marble) which may either be of a pure white or be colored with iron or manganese oxides, or be black from the presence of bituminous matter. It also occurs in large six-sided crystals as arragonite, and in rhombohedral crystals as Iceland or calc spar, etc.

In the *animal* kingdom it occurs as pearls, and forms the chief constituent of corals, fish, and egg-shells. It enters largely into the formation of bone.

Properties.—A white, crystalline or amorphous body. It is dimorphous, crystallising in rhombohedra (Sp. gr. 2·7) as in calcite, and in rhombs (Sp. gr. 3·2) as in arragonite. It is almost insoluble in pure water (2 grs. in 1 gallon), but soluble in water (as $CaH_2,2CO_3$) containing carbonic anhydride, from which solution $CaCO_3$ is deposited as the CO_2 is given off. A saturated carbonic acid water at 50° F. will dissolve about 60 grains of $CaCO_3$ per gallon. Thus are formed the stalactites and stalagmites of Derbyshire, and the tufa and travertine of volcanic districts. It undergoes decomposition (*dissociation*) when heated in air ($CaCO_3 = CaO + CO_2$), but may be raised to a white heat in an atmosphere of carbonic anhydride without change. It is also decomposed by the action of hydrochloric, nitric, sulphuric and other acids.

It constitutes one and the chief cause of the *temporary hardness* of water—that is, the hardness removable by boiling (*see* p. 247). The deposition of the lime and magnesium carbonates in boilers, constitutes what is called "furring," and renders a water containing an excess of such constituents unsuitable for boiler purposes. The deposition, however, may, in a great measure, be prevented by the addition to the water of a little soda ash or ammonium chloride. In the latter case, ammonium carbonate is formed, which volatilises along with the steam, a soluble calcium chloride remaining. Dr. Clark suggested a plan of softening hard waters by adding a sufficient quantity of lime to combine with the carbonic acid holding the carbonate of lime in solution, whereby the calcium carbonate pre-existent in the water, together with that formed by the union of the carbonic acid and the added lime, are precipitated together. (Clark's process.)

Calcium carbonate constitutes the basis of many building materials, such as marble, Portland stone, Bath stone, and magnesian limestone of which the Houses of Parliament are built. The decay of such stones in a town is dependent on the action of the sulphur acids (produced by burning coal, etc.), and of carbonic acid, as well as on the mechanical disintegration occasioned by the expansion of the water in the pores of the stone during freezing.

(17-18.) Calcium Phosphates.—The *Tricalcium phosphate* (Ca_32PO_4) occurs native in *osteolite*, *coprolite*, etc. It is the principal ingredient of bone-ash. Various calcium phosphates known as *phosphorite*, *apatite*, etc., have been found native. $CaHPO_4,2H_2O$ occurs native as *brushite*. A *pyrophosphate* ($Ca_2P_2O_7$) and *metaphosphate* ($Ca2PO_3$) are known. *Calcium superphosphate* ($Ca''H_4,2PO_4$) is formed when bone-earth is treated with oil of vitriol.

(20.) Calcium Oxalate ($CaC_2O_4,2H_2O$) is a white, insoluble body, precipitated when ammonium oxalate is added to a lime solution. It is insoluble in acetic acid, but is converted by heat into calcium carbonate ($CaC_2O_4 = CaCO_3 + CO$).

Calcium Hypochlorite ($CaCl_2O_2$).—Prepared by passing chlorine into milk of lime.

Chloride of Lime, or "*Bleaching powder*," is prepared by passing chlorine over slaked lime. The lime absorbs nearly half its weight of chlorine. The commercial product contains 20 to 35 per cent. of *available* chlorine (*i.e.*, of chlorine capable of being given off when the powder is heated with sulphuric acid ($CaCl_2O + H_2SO_4 = CaSO_4 + H_2O + Cl_2$.) Formerly this compound was regarded as a mixture of calcium chloride and hypochlorite. Thus—

$$\begin{array}{ccccccc} 2CaH_2O_2 & + & 2Cl_2 & = & \underbrace{CaCl_2 \;+\; CaCl_2O_2} & + & 2H_2O. \\ \text{Calcic hydrate} & + & \text{Chlorine} & = & \text{Bleaching powder} & + & \text{Water.} \end{array}$$

But inasmuch as bleaching powder is neither *deliquescent* (when well made) nor *soluble in alcohol* as calcium chloride is, it is believed to be a definite chemical combination, viz., a calcium-chlorohypochlorite, $Ca(ClO)Cl$.

The hypochlorite is decomposed by water, by heat (oxygen being evolved and $CaCl_2$ formed), by moist air (hypochlorous acid being evolved) and by acids. Its solutions evolve oxygen when heated with certain metallic hydrates. Heated in a closed vessel, it decomposes.

In employing it for bleaching, the material is first passed through a solution of the bleach, and afterwards into very dilute hydrochloric or sulphuric acid, hypochlorous acid being by this means liberated.

Reactions of Lime Compounds.

The salts are colorless (unless the acid be colored).

Non-luminous Flame, colored yellowish red.

Spectrum.—Several bands in green, yellow, and orange, the one in the green and the one in the orange being those specially characteristic.

Alkaline Carbonates.—White ppt. of $CaCO_3$.

Sulphuric Acid and *Soluble Sulphates.*—White ppt. of $CaSO_4$ in strong solutions, the precipitation in the case of weak solutions only occurring when alcohol has been added.

Calcium Sulphate.—No precipitate.

Ammonium Oxalate.—White ppt. of CaC_2O_4, soluble in HCl and HNO_3; insoluble in ammonia, in oxalic or in acetic acids.

Potassium Chromate.—No ppt. (*See* Barium, p. 377.)

MAGNESIUM (Mg'').

Atomic weight, 24. *Specific gravity,* 1·743. *Specific heat,* 0·25. *Atomicity, dyad* ($MgCl_2$). ***Fuses and volatilises at a red heat.***

[Its general properties, the volatility of its chloride, the solubility of its sulphate, and the isomorphism of its compounds with those of zinc, ally it, so far as its general chemistry is concerned, to zinc rather than to the metals of the earths. We consider it here for convenience.]

History.—Isolated by Davy in 1808.

Natural History.—It occurs (*a*) in the *mineral* kingdom as magnesite ($MgCO_3$), dolomite or magnesian limestone ($Ca''Mg''2CO_3$), as brucite (MgH_2O_2), as a sulphate in Kieserite and in Epsom salts ($MgSO_4,H_2O$); and as boracite, hydroboracite, and pearl spar. As a *silicate* it is found in the form of mica, asbestos, hornblende, serpentine, olivine, steatite (soapstone or French chalk), meerschaum, talc, etc. It occurs in most waters as a carbonate and a sulphate. (β.) It is found in *animals* and *vegetables* in combination with carbonic, phosphoric, and organic acids.

Preparation.—(1.) By the electrolysis of fused magnesium chloride. (Davy.)

(2.) By heating magnesium chloride with metallic potassium or sodium. (Bussy.)

(3.) By fusing a mixture of magnesium chloride ($MgCl_2$), sodium chloride ($NaCl$), calcium fluoride (CaF_2) (*fluorspar*) and sodium. The mixture is to be stirred with an iron rod. On cooling, the magnesium forms in large globules, and may be purified by distillation.

Properties.—(*a.*) *Physical.* A white, hard, light, malleable, ductile metal, melting at a red heat, and sufficiently volatile to be distilled if heated in a hydrogen atmosphere. Sp. gr. 1·743. It is insoluble in cold water, but is soluble in acidulated water and in ammonium chloride ($4NH_4Cl + Mg = 2NH_4Cl,MgCl_2 + H_2 + 2NH_3$).

(β.) *Chemical.* It decomposes warm, but not cold, water. (It is said that the pure metal does not act on water even at 212° F. (100° C.).) It is not easily affected by *dry* air, but rapidly oxidizes in *moist* air at ordinary temperatures. It burns in air (forming MgO), the light evolved being of great intensity and highly actinic :—hence its use in photography. It also burns in chlorine, and in bromine, iodine, and sulphur vapors. It combines with nitrogen at high temperatures to form a nitride (N_2Mg_3). Dilute acids dissolve it with the evolution of hydrogen. It ignites when introduced into hydrochloric acid gas, but is not acted on by cold nitro-sulphuric acid. With solutions of caustic alkalies, it does not (like zinc) evolve hydrogen, MgH_2O_2 not being soluble in the alkali. It reduces acid solutions of salts of many of the metals, hydrogen gas (or in the case of arsenical and antimonial compounds being present, arseniuretted or antimoniuretted hydrogen) being evolved. With ammonia salts it evolves hydrogen, a magnesium ammonic salt being formed.

Uses.—It is used as a source of light in photography, the magnesium spectrum being continuous, and the light of high actinism.

Compounds of Magnesium ($Mg = 24$).

	COMPOUNDS.	Formula.	Molecular Weight of Anhydrous Compound.	Specific Gravity of Crystals.
1	Magnesium oxide	MgO	40	3·2
2	,, hydrate	MgH_2O_2		
3	,, chloride	$MgCl_2,6H_2O$	95+108	1·562
4	,, bromide	$MgBr_2$	184	
5	,, iodide	MgI_2		
6	,, fluoride	MgF_2		
7	,, nitride	Mg_3N_2.		
8	,, boride	Mg_3B_2		
9	,, silicide	Mg_2Si		
10	,, sulphide	MgS	56	
11	,, sulphhydrate ..	MgH_2S_2		
12	,, sulphate (Epsom salts)	$MgSO_4,7H_2O$	120+126	1·660
13	,, nitrate	$Mg2NO_3,6H_2O$	148+108	1·464
14	,, carbonate ..	$MgCO_3$.	84	3·056
	(basic carbonate)	$3MgCO_3,MgH_2O_2 3H_2O$		
15	,, borate	$3MgO,B_2O_3$		
16	,, arsenate	$Mg_3As_2O_8$		
17	,, hydric arsenate	$MgHAsO_4,7H_2O$		
18	,, ammonic arsenate	$MgNH_4AsO_4,6H_2O$		
19	,, silicates	various		
20	,, hydric phosphate (ortho)	$HMg''PO_4,7H_2O$		
21	,, ammonic phosphate (triple phosphate) ..	$Mg''_2(H_4N)_2 2PO_4,12H_2O$	274	
22	,, pyrophosphate .	$Mg_2P_2O_7$	222	
23	,, phosphate (ortho)	$Mg_3P_2O_8$		

(1.) **Magnesium Oxide,** *Magnesia Calcinata or Usta* (MgO). This is the only oxide of magnesium. It occurs native as *periclase.*

Preparation.—It may be prepared by burning magnesium in air, or by igniting magnesium carbonate or nitrate in a crucible ("magnesia usta," "calcined magnesia"). It is a white and almost insoluble powder (1 part in 55,000 times its weight of water). Sp. gr. 3·07 to 3·61. It fuses in the oxyhydrogen flame. Like lime, baryta, and strontia, it slakes with water; but, unlike them, it develops no very perceptible heat in doing so. The magnesium hydrate (MgH_2O_2) thus formed, slowly absorbs atmospheric carbonic anhydride. The hydrate forms a compact mass like plaster of Paris, and may be used for casts. Magnesium oxide, when placed on turmeric paper and moistened, turns the paper brown.

(2.) **Magnesium Hydrate** (MgH_2O_2) occurs in nature as brucite. It may be prepared as a white powder (in addition to the method mentioned above), by precipitating magnesium sulphate with potassium hydrate ($MgSO_4+2KHO = K_2SO_4+MgH_2O_2$). It is insoluble in water, and infusible by heat. It absorbs CO_2 from the air. It is decomposed by heat into MgO and H_2O.

(3.) **Magnesium Chloride** ($MgCl_2$) is found in salt deposits and in sea water. It may be prepared by acting on the metal, its oxide or carbonate, with hydrochloric acid. On evaporation, the solution of $MgCl_2$ formed is decomposed into MgO and HCl, but if ammonium chloride be added to the solution before it is evaporated, the double salt ($MgCl_2,2NH_4Cl$) is formed, from which the NH_4Cl may be volatilized, leaving the pure $MgCl_2$ in a fused state in the crucible.

It is a crystalline deliquescent substance, freely soluble in water and in alcohol. It volatilizes at a red heat. It combines with the oxide to form various *oxychlorides.* A paste of magnesia and magnesium chloride forms within a few hours a mass sufficiently hard to be polished.

It forms numerous double compounds, of which ($MgCl_2,KCl,6H_2O$) (carnallite), ($MgCl_2$, NH_4Cl, $6H_2O$) and ($2MgCl_2,CaCl_2$, $12H_2O$), (tachydrite), are illustrations.

(4.) **Magnesium Bromide** ($MgBr_2$) and **Iodide** (MgI_2) are found in sea water and in saline springs.

(6.) **Magnesium Fluoride** (MgF_2) forms double compounds, of which MgF_2,NaF is an illustration.

(7.) **Magnesium Nitride** (Mg_3N_2) may be produced by the direct union of nitrogen and the metal. It is a crystalline body, easily decomposed by water ($Mg_3N_2+3H_2O = 2NH_3+3MgO$).

(10.) **Magnesium Sulphide** (MgS) is prepared by heating the metal to redness in sulphur vapor, or by passing CS_2 vapor over red-hot MgO. It is decomposed by water into MgH_2O_2 and MgH_2S.

Magnesium Sulph-hydrate may be prepared by passing H_2S through water containing magnesia in suspension.

(12.) **Magnesium Sulphate** (*Epsom salts*) ($MgSO_4,7H_2O$), is found in most waters, but especially in certain springs about Epsom. It occurs in certain salt beds as kieserite.

Preparation.—By the calcination of dolomite ($MgCa2CO_3$), a residue is formed of MgO and CaO. This, after washing to extract some of the lime, is acted on with sulphuric acid, whereby $MgSO_4$ and $CaSO_4$ are formed, the latter of which, being insoluble, is precipitated. The magnesium sulphate may then be obtained from the clear solution by evaporation.

It may also be prepared from the " bittern " of sea water—that is, the liquor remaining after the extraction of the common salt. It may also be prepared from kieserite, by first treating it with water to dissolve out the common salt present. Lastly, it may be obtained from the liquor of the alum works.

Properties.—A white crystalline, slightly efflorescent salt (right rhombic prisms), of a bitter taste. It is soluble in water (1 in 3 aq. at

60° F., and 1 in 1·5 aq. at 212° F.). At a heat of 212° F. (100° C.) it fuses in its water of crystallization, becoming $MgSO_4,H_2O$. At about 482° F. (250° C.) it becomes $MgSO_4$, which at a red heat fuses without decomposition. The seventh molecule of water (water of constitution) in the salt $MgSO_4,H_2O$ may be displaced by a molecule of an anhydrous alkaline sulphate (such as K_2SO_4), a double salt resulting (such as $MgSO_4,K_2SO_4,6H_2O$), which has the same crystalline form as magnesium sulphate.

(14.) **Magnesium Carbonate** ($MgCO_3$).—*Natural History.* Found native as magnesite and (together with $CaCO_3$) as dolomite.

Preparation.—Boiling solutions of K_2CO_3 and $MgCl_2$ are mixed together, and the precipitate formed dissolved in carbonic acid water. From this solution, the salt ($MgCO_3,3H_2O$) is deposited as the carbonic anhydride escapes. A compound with five molecules of water has been prepared. "Magnesia alba" ($3MgCO_3,H_2O,MgH_2O_2$ or possibly $3MgCO_3$, MgH_2O_2, $3H_2O$?) is prepared by precipitating a magnesium sulphate solution with one of sodium carbonate.

Compounds of the carbonate of magnesia with carbonates of lime, potash, and ammonia are known (*e.g.*, $MgCO_3,K_2CO_3,4H_2O$).

(19.) The **Magnesium Silicates** are numerous. Talc ($4MgO, 5SiO)_2$, steatite ($3MgO,4SiO_2$), meerschaum ($2MgO,3SiO_2,2H_2O$), and serpentine ($MgO,2SiO_2$), are a few illustrations of its more common natural forms.

Phosphates.—The orthophosphate Mg_32PO_4 is found in bones and seeds. The other orthophosphates that have been prepared are ($MgHPO_4,7H_2O$), ($MgKPO_4,H_2O$), ($MgNaPO_4,9H_2O$), and ($MgNH PO_4,6H_2O$), etc.

(21.) **Ammonium Magnesic Phosphate** (*Triple Phosphate*) ($MgNH_4PO_4,6H_2O$) is an important salt, magnesia being usually precipitated on analysis in this form. It is insoluble in water containing free ammonia. On igniting the salt, magnesic pyrophosphate ($Mg_2P_2O_7$) is formed, the compound commonly employed in the quantitative estimation of magnesia.

Triple phosphate is a frequent constituent of urinary calculi.

REACTIONS OF MAGNESIUM COMPOUNDS.

The salts are colorless unless the acid be colored.

Non-luminous flame.—No coloration.

Spectrum.—Lines in the green.

Alkaline and Barium Hydrates.—Ppt. (gelatinous) of MgH_2O_2, insoluble in excess. [N.B.—No precipitate is formed in the cold when ammonia or salts of ammonia are present, because of the formation of ammonium magnesic salts.]

Sodium Carbonate; ppt. of a basic carbonate (Ammonium salts prevent precipitation).

Ammonium Phosphate; A. white ppt. of $MgNH_4PO_4$, insoluble in aqueous ammonia.

CHAPTER XV.

THE METALS—(*continued*).

MANGANESE (Mn).

Atomic weight 55. Atomicity, dyad to octad. Dyad, in manganous compounds (MnO), *and a pseudo-triad in manganic compounds, where the compound contains two triad atoms of manganese in the molecule, the double atom of the metal being therefore sexvalent* ($Mn_2'''O_3$). *Specific gravity* 8·0. *Melts at a white heat.*

History.—Manganese was used from very early times to color glass. The oxide was recognised by Scheele in 1774, and the metal obtained by Gahn in 1780.

Natural History.—Manganese is not found in a free state. It occurs as an *oxide* in *hausmannite* (Mn_3O_4), *braunite* (Mn_2O_3), and *pyrolusite* (MnO_2), as a *sulphide* in *manganese blende* (MnS), as a *carbonate* in *manganese spar* ($MnCO_3$), and as a *silicate* in *red manganese ore* ($MnSiO_3$). It is found in the ashes of plants and of animals, and is a widely diffused metal.

Preparation.—(1.) By reducing manganous carbonate with charcoal.

(2.) By the electrolysis of an aqueous solution of manganous chloride.

(3.) By the action of sodium on manganous fluoride or chloride.

(4.) By reducing the oxide with carbon in a crucible of caustic lime. (Deville.) (The oxide cannot be reduced with hydrogen.)

Properties.—(*a.*) *Physical.* A greyish-white or reddish metal, brittle, but so extremely hard that it will scratch steel. It is feebly magnetic, and very difficult to fuse. Sp. gr. 8·00.

(*β.*) *Chemical.* It is readily oxidized when exposed to the air, and has to be preserved under naphtha. It decomposes water at ordinary temperatures, liberating hydrogen. It has a great attraction for carbon. It is soluble in dilute acids.

Uses.—It is mixed with iron for the purpose of increasing hardness.

Compounds of Manganese (Mn = 55).

		SALTS.	Ordinary Formula.	Molecular Weight, Anhydrous.	Specific Gravity.	Mn per cent.
1	Oxides.	Manganous oxide	$Mn''O$	71	5.18	77·46
2		,, hydrate	MnH_2O_2	89		61·79
3		Manganic oxide (sesquioxide)	$Mn'''_2O''_3$	158	4·82	69·62
4		Trimanganic tetroxide or red oxide	Mn_3O_4	229	4·72	72·05
5		Manganic dioxide (peroxide)	$Mn^{iv}O_2$	87	4·94	63·22
6		,, anhydride	$Mn^{vi}O_3$ (?)	103		53·39
6*a*		,, acid	H_2MnO_4 (?)			
7		Permanganic anhydride	$Mn^{vii}_2O_7$	222		
7*a*		Permanganic acid	$HMnO_4$	120		
8	Chlorides.	Manganous chloride	$MnCl_2$	126	2·01	43·65
9		Manganic chloride	$MnCl_4$	197		27·91
10		Dimanganic hexachloride	Mn_2Cl_6	323		34·05
11		Manganic oxychloride	MnO_3Cl			
12		Manganous bromide	$MnBr_2$			
13		,, iodide	MnI_2			
14		,, fluoride	MnF_2			
15		,, perfluoride	MnF_4			
16		Manganous sulphide	MnS	87		
17		Manganic sulphide	MnS_2			
18		Manganous carbonate	$MnCO_3$	115		47·82
19		,, sulphate	$MnSO_4,7H_2O$	151+126	3·1 of anhyd.	36·42
20		Manganic sulphate	Mn_23SO_4			
21		Manganese alum	$Mn_2K_24SO_424H_2O$			
22		Manganous dithionate	$MnS_2O_6,3H_2O$			
23		,, silicate	$MnSiO_3$			
24		,, nitrate	$Mn2NO_3,6H_2O$	179+108	1·8	

COMPOUNDS OF MANGANESE AND OXYGEN.

Manganous oxide	MnO.
Manganic oxide	Mn_2O_3.
Trimanganese tetroxide	Mn_3O_4.
Manganese dioxide (peroxide) ...	MnO_2.
Manganic anhydride (?)	MnO_3.
Permanganic anhydride (?)	Mn_2O_7.

MnO, Mn_2O_3, and MnO_2 have been prepared ; MnO_3 and Mn_2O_7 have never been isolated.

Chemically, it is to be noted that—

MnO is a powerful base.

Mn_2O_3 is feebly basic.

$\left.\begin{matrix} Mn_3O_4 \\ MnO_2 \end{matrix}\right\}$ are indifferent oxides, that is, neither basic nor acid.

$\left.\begin{matrix} MnO_3 \\ Mn_2O_7 \end{matrix}\right\}$ are anhydrides.

(1.) **Manganous Oxide,** *Protoxide of Manganese* (MnO). Sp. gr. of the native oxide 5·18; of the artificial, 4·7 to 5·0.

Preparation.—(1.) *Anhydrous.* (Found native as *manganosite.*) By igniting manganous carbonate or the higher oxides in a current of hydrogen.

(2.) As a *hydrate* (found native as pyrochroit) (MnH_2O_2). (*Manganous hydroxide*). By the addition of an alkali to the solution of a manganous salt.

Properties.—Manganous oxide is found of various tints—olive green, dark green, or emerald green, accordingly as it is prepared. Prepared at low temperatures, it rapidly becomes converted into the red oxide (Mn_3O_4). It is soluble in a solution of NH_4Cl with the evolution of NH_3, and in HCl without the evolution of Cl. *Manganous hydrate* (MnH_2O_2) is in the first instance white, but rapidly turns brown on exposure to air, being converted into Mn_2O_3,H_2O when free from alkali, and into MnO_2,H_2O in the presence of an alkali. It is a powerful base. Its salts are flesh-colored, and isomorphous with ferrous salts.

(3.) **Manganic Oxide,** *Sesquioxide of Manganese* (Mn_2O_3).

Natural History.—Found native as *braunite* (Mn_2O_3), and as *manganite* (Mn_2O_3,H_2O).

Preparation.—(1.) *Anhydrous.* By heating any oxide of manganese in oxygen, or by carefully heating the hydrate.

(2.) As a *hydrate,* $Mn_2H_2O_4$.—By first passing chlorine through water in which manganous carbonate ($MnCO_3$) is suspended, and subsequently removing any excess of manganous carbonate with dilute nitric acid.

Properties.—A brown substance, decomposed by heat ($6Mn_2O_3 = 4Mn_3O_4 + O_2$). It colors glass violet (amethyst). It is a weak base, and isomorphous with alumina and ferric oxide. Its salts are red, and are decomposed by heat. Strong sulphuric acid when heated, decomposes it, liberating oxygen, and forming a manganous sulphate; dilute sulphuric acid dissolves it; nitric acid decomposes it into MnO and MnO_2, the acid dissolving the former oxide; hydrochloric acid evolves chlorine when heated with it.

Manganic hydrate ($Mn_2H_2O_4$) is a reddish brown powder, which if heated to redness yields Mn_3O_4. When heated with sulphuric acid to 212° F. (100° C.) it forms manganic sulphate, no oxygen being evolved. It is insoluble in dilute sulphuric acid.

(4.) **Red Manganese Oxide**; *Mangano-Manganic-Oxide, Trimanganic tetroxide* ($Mn_3O_4 = MnO,Mn_2O_3$) occurs native as "hausmannite," and may be prepared by heating any manganese oxide in the air. It is, in short, that oxide which, by the absorption or giving out of oxygen, is formed when the other oxides are strongly heated.

Heated in hydrogen, it becomes MnO; heated in oxygen, it is converted into Mn_2O_3.—It forms a hydrate of uncertain composition.

Mn_3O_4 is soluble in HCl, with evolution of chlorine and the formation of $MnCl_2$ ($Mn_3O_4+8HCl=3MnCl_2+Cl_2+4H_2O$). Boiled in a solution of ammonium chloride, MnO is dissolved, leaving a residue of Mn_2O_3.

It does not form salts. Acted upon with dilute oxy-acids, a manganous salt (*i.e.*, a salt of manganous oxide) results, an insoluble residue of manganese dioxide remaining ($Mn_3O_4+4HNO_3=Mn2NO_3+MnO_2+2H_2O$).

Fused borax and glass dissolve it, acquiring an amethyst color.

(5.) **Manganese Dioxide**; *Binoxide*, *Peroxide*, or *Black Oxide of Manganese* (MnO_2).

Natural History.—Found native in a crystalline state as "pyrolusite," and in an amorphous form as "psilomelane." It occurs as a hydrate in "wad" and "varvicite" ($Mn_2O_3,2MnO_2,H_2O$).

Preparation.—(1.) *Anhydrous.* By calcining manganous nitrate ($Mn2NO_3 = MnO_2+N_2O_4$).

(2.) As a *hydrate.* (*a.*) By acting on potassium permanganate with an acid.

(β.) By heating Mn_3O_4 or Mn_2O_3 with nitric acid.

(γ.) By adding chloride of lime (hypochlorite) to a solution of a manganous salt.

Properties.—(*a.*) *Physical.* A black substance, insoluble in water. It is a good conductor of electricity. Undergoes decomposition in air at a red heat ($3MnO_2 = Mn_3O_4+O_2$). Heated in oxygen it forms Mn_2O_3, and in hydrogen MnO.

(β.) *Chemical.* MnO_2 is an "indifferent" oxide, that is, it is neither acid nor basic. It is soluble in dilute acids in the cold in the presence of oxidisable bodies (such as oxalic acid). Heated with *sulphuric acid* oxygen is evolved, and a manganous sulphate formed ($2MnO_2+2H_2SO_4=2MnSO_4+2H_2O+O_2$). With hot *hydrochloric acid* chlorine is set free, and $MnCl_2$ formed. *Nitric acid* has no action upon it.

Hydrated manganese dioxide (MnH_2O_3) is a black powder. It possesses acid properties, reddening litmus, and expelling CO_2 from solutions of alkaline carbonates. It forms a certain class of compounds, called *manganites.*

Manganese dioxide is employed to obtain a colorless glass. It is largely used in the preparation of the chlorine required in the manufacture of bleaching-powder. Inasmuch as MnO_2 usually contains iron, the residual liquor also contains mixed manganous and ferric chlorides. From this mixture the manganous chloride may be again converted into oxide by the addition of a little lime, which precipitates the *per*-chloride of iron without decomposing the protochloride of manganese, peroxides being weaker bases than protoxides (Fe_2Cl_6+

$3CaO = Fe_2O_3 + 3CaCl_2$). The manganese as a carbonate might be thrown down from the solution with chalk ($MnCl_2 + CaCO_3 = MnCO_3 + CaCl_2$). If this be roasted at 600° F., the MnO_2 will be reproduced. (Dunlop.)

Weldon's process for the regeneration of Manganese Dioxide.—This process has for its purpose the recovery of the manganese dioxide from the waste liquor of the chlorine retorts. This liquor consists of an acid solution of the chlorides of iron and manganese, together with other impurities (pp. 88 and 89). Calcium carbonate is first added to neutralize any free acid and to precipitate the iron. To the clear solution of lime and manganese chlorides, milk of lime is added, in the proportion of 1·5 mols. of CaH_2O_2 to every one mol. of $MnCl_2$. This mixture is now heated by steam to about 167° F. (75° C.), after which air is blown through the liquid. The manganous hydrate (MnO,H_2O), *in the presence of a basic oxide*, is oxidized to the peroxide (MnO_2), which, combining with the basic oxide, yields a calcic manganite ($CaO, 2MnO_2$). The precipitate produced (manganese mud), consisting of lime mixed with from 30 to 35 per cent. of MnO_2, is collected and pressed into a cake, which is then used for the preparation of fresh chlorine by acting upon it with hydrochloric acid.

NOTE.—Two cubic metres of air are required for every 1lb. of MnO_2 recovered, the time occupied in the process being at the rate of five hours per ton. About 80 per cent. of the manganese used may be recovered by this process.

(6.) Manganic Acid (H_2MnO_4).—The Manganates.

Neither the free acid nor manganic anhydride is known. *Potassium manganate* (mineral chameleon) (K_2MnO_4) and *sodium manganate* (Na_2MnO_4) may be prepared by fusing together caustic potash or soda respectively, with manganese dioxide. The solutions when evaporated *in vacuo* over sulphuric acid yield green crystals of the manganate. When these crystals are dissolved in pure water, or in water containing a trace of acid (the manganates being less stable in an acid than in an alkaline solution), the salts are decomposed, the color of the liquid changing from green to red, (due to the formation of potassium or sodium permanganate,) a black precipitate of manganese dioxide being thrown down ($3K_2MnO_4 + 2H_2O = K_2Mn_2O_8 + MnO_2 + 4KHO$). A solution of sodium manganate constitutes "*Condy's green disinfecting fluid*," the action of which depends upon the ease with which the manganates yield their oxygen to organic matter.

"Cassel green" is a barium manganate ($Ba''MnO_4$), prepared by fusing MnO_2 with barium nitrate, and extracting the product with water.

(7.) Permanganic Acid ($H_2Mn_2O_8$).—The Permanganates.

Permanganic acid is only known in solution.

Preparation of permanganic anhydride (Mn_2O_7).—(1.) A potassium permanganate is formed by the action of heat on an intimate mixture of manganese dioxide (4 parts), potassium chlorate (3·5 parts). and potassium hydrate (5 parts), a potassium manganate being formed, which may be dissolved out of the residue with boiling water. Carbonic anhydride is then passed through the green solution, until it becomes red ($3K_2MnO_4 + 2CO_2 = K_2Mn_2O_8 + 2K_2CO_3 + MnO_2$). The clear liquid is then decanted from the precipitate, and evaporated to a small bulk, from which solution potassium permanganate may be crystallised (Béchamp). By treating the crystals with sulphuric acid (care being taken that the crystals are free from chlorine and the acid pure, otherwise a dangerous explosion may occur), permanganic anhydride rises as a violet vapor, and may be condensed to a dark liquid.

(2.) A solution of the acid may also be prepared by decomposing barium permanganate with dilute sulphuric acid.

Properties.—Permanganic anhydride is a reddish brown, unstable, oily liquid. It explodes when heated, and decomposes (giving off oxygen) at ordinary temperatures. It is very hygroscopic. Great heat is produced, with decomposition of some of the oxide, when it is dissolved in water. The solution is violet-colored.

The ammonium salt ($(NH_4)_2Mn_2O_8$ is prepared by the action of ammonic sulphate on the barium salt; the barium salt ($Ba''Mn_2O_8$) by the action of CO_2 on barium manganate; and the argentic salt ($Ag_2Mn_2O_8$) by precipitating a solution of potassium permanganate with nitrate of silver.

The permanganates are not so unstable as the manganates, nevertheless they readily yield their oxygen to organic matter (*Condy's red disinfecting liquid*). Under such conditions the permanganic acid first becomes manganic acid, the manganese being ultimately reduced to the state of hydrated manganese dioxide (MnO_2, H_2O).

Potassium permanganate crystals appear red by transmitted, and dark green by reflected light. The permanganates are isomorphous with the perchlorates. When heated they yield oxygen, a manganate being formed ($K_2Mn_2O_8 = K_2MnO_4 + MnO_2 + O_2$). Boiled with a caustic alkali they also evolve oxygen, becoming manganates ($K_2Mn_2O_8 + 2KHO = 2K_2MnO_4 + H_2O + O$). All the permanganates (excepting the silver salt) are soluble in water, their solutions being of a red colour. This colour is discharged by sulphurous acid, by neutral solutions of the sulphides and pentathionates, by acid solutions of the sulphates, thiosulphates, arsenites, nitrites, etc., and by acid solutions of mercurous, ferrous, stannous, and antimonious salts, the permanganic acid being reduced to the colorless manganous oxide (*Mineral Chameleon*).

(8.) **Manganous Chloride**; *Protochloride of Manganese* ($MnCl_2$).

Preparation.—It is formed when the metal is burnt in chlorine, or the oxide heated in dry HCl gas. It occurs (mixed with ferric chloride) in the residual liquor obtained during the preparation of chlorine

(p. 88). From this liquor it may be prepared by evaporating the clear filtrate to dryness and igniting, by which means the iron salt is either volatilized or converted by the remaining water into an insoluble sesquioxide. On treating the mass thus formed with water, the manganous chloride may be dissolved out. Another method for its preparation is to precipitate a part of the solution with sodium carbonate, and to employ the manganese carbonate so formed to precipitate the iron ($Fe_2Cl_6 + 3MnCO_3 + 3H_2O = Fe_2H_6O_6 + 3MnCl_2 + 3CO_2$).

Properties.—A pink, deliquescent salt, soluble in water and in alcohol, and fusible at a red heat.

(9.) **Manganic Chloride** (Mn_2Cl_6), a brown substance decomposed by heat ($Mn_2Cl_6 = 2MnCl_2 + Cl_2$), and *Manganic Tetrachloride* ($MnCl_4$) are only known in solution.

(11.) **Manganic Oxychloride** (MnO_3Cl) is prepared by adding sodium chloride to potassic permanganate dissolved in sulphuric acid. A brown explosive liquid. It is decomposed by water into permanganic and hydrochloric acids, which by their mutual action yield Cl and MnO_2.

(16.) **Manganous Sulphide** (MnS) occurs native as "manganese blende."

Preparation.—(1.) (*As a hydrate,* MnS, H_2O.) By the action of an alkaline sulphide on a solution of a manganous salt. (2.) (*Anhydrous.*) By heating one of the manganese oxides in a current of H_2S.

Properties.—The hydrate prepared by process 1 is flesh-colored and amorphous, soluble in dilute acetic and other acids with evolution of H_2S, and turns brown by exposure. The anhydrous sulphide prepared by process 2 is a greenish black powder.

Manganous sulphide forms double compounds with alkaline sulphides (*e.g.*, $K_2S,3MnS$).

(17.) **Manganic Sulphide** (MnS_2) occurs native in a crystalline form.

Oxy-Salts.

(18.) **Manganous Carbonate** ($MnCO_3$) is found native as "manganese spar." It may be prepared as a hydrate ($2MnCO_3,H_2O$) by precipitating $MnCl_2$ with an alkaline carbonate. It rapidly oxidises by exposure.

(19.) **Manganous Sulphate** ($MnSO_4$).

Preparation.—Manganese dioxide is treated with sulphuric acid, the solution evaporated to dryness, and the residue ignited in order to decompose any ferric sulphate present. By acting on this residue with water, pure manganese sulphate may be dissolved out, leaving the insoluble ferric oxide. The salt obtained contains 7 or 5 molecules of water, according to the temperature at which the crystals have been prepared. At 392° F. (200° C.) the salt becomes anhydrous. It forms double sulphates with alkaline sulphates.

Properties.—A rose-colored soluble salt, used by the dyer in producing blacks and browns.

(20.) **Manganic Sulphate** (Mn_23SO_4) is a green powder prepared by acting on hydrated manganese dioxide with sulphuric acid. Decomposes at 320° F. (160° C.) with evolution of oxygen.

(21.) If K_2SO_4 [or$(NH_4)_2SO_4$] be added to a solution of manganic sulphate, **Manganese Alum** is formed [$K_2SO_4,Mn_23SO_4,24H_2O$]. This is not to be confounded with the manganese aluminium alum ($MnSO_4,Al_23SO_4,24H_2O$), which is a pseudo-alum, where one of a dyad (Mn'') has replaced two of a monad metal (such as K'), the salt possessing a different crystalline form to that of the class known as "alums."

(24.) **Manganous Nitrate** ($Mn_2NO_3,6H_2O$) is prepared by the action of nitric acid on the carbonate. It undergoes decomposition by heat.

REACTIONS OF MANGANESE.

Salts.—Colored.

Spectrum.—Lines in green and yellow. Spark spectrum ;—lines numerous.

Fused with Nitre and Sodium Carbonate.—A green mass of alkaline manganate.

Borax bead.—Amethyst color in oxidizing flame ; no color in reducing flame.

Caustic Alkalies.—A white ppt. (MnH_2O_2), turning brown.

Ammonia.—Imperfect ppt. of MnH_2O_2. [No ppt. in presence of NH_4Cl.]

Alkaline Carbonates.—Ppt. of $MnCO_3$.

Ammonium Sulphide.—Flesh-colored ppt. of hydrated sulphide, soluble in dilute acids.

IRON ($Fe''=56$).

Atomic weight, 56. *Specific gravity,* 7·8. *Atomicity dyad* ($''$), *as in ferrous salts* ($Fe''Cl_2$; $Fe''SO_4$) *and hexad* (^{vi}) (i.e., *the double triad atom of iron in the molecules renders the metal sexvalent*) *in ferric salts* (Fe_2O_3).

History.—Known to the ancients.

Natural History.—Found *native,* together with Ni, Co, Mn, Cu, etc., in meteorites. It is also found accompanying platinum ores. In *combination* it occurs in great abundance in numerous ores, as follows :—

Iron Ores.

IRON ORES. Common Names—Locality.	Composition.	Specific Gravity.
Magnetic iron ore; Loadstone; Iron-sand (India)	Fe_3O_4	5·09
Red hæmatite (Cornwall). (*Red ochre* contains clay)	Fe_2O_3	5·0
Specular iron; Fer oligiste; Iron glance (Elba, Russia, Sweden)		5·2
Brown hæmatite; Pea iron ore; yellow ochre; limonite (France)	$2Fe_2O_3,3H_2O$	3·9
Spathic iron ore (Saxony)	$FeCO_3$	3·8
Clay ironstone (Great Britain, America) ..	$FeCO_3$, with clay.	2·7 to 3·47
Black-band (Scotland)	$FeCO_3$, with bituminous matters (20 to 30 per cent.)	
Iron pyrites	FeS_2	
Siliceous ironstone (Northampton) ..	Fe_2O_3 and $FeCO_3$	
Bog iron ore	$2Fe_2O_3,3H_2O$, and a ferric phosphate.	

The following table from Bloxam, compiled from analyses given in Percy ("On Iron and Steel") shows the composition of most of the English iron ores:—

In 100 parts.	Iron.		Oxide of Manganese.		Phosphoric Acid.		Bisulphide of Iron.		No. of samples analysed.
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	
Clay ironstone from coal measures ..	43·30	20·95	3·30	0·46	1·42	0·07	1·21	..	77
Clay ironstone from the Lias	49·17	17·34	1·30	..	5·05	..	1·60	..	12
Brown hæmatite ..	63·04	11·98	1·60	trace	3·17	..	0·30	..	23
Red hæmatite ..	69·10	47·47	1·13	trace	trace	trace	0·06	..	5
Spathic ore	49·78	13·98	12·64	1·93	0·22	..	0·11	..	6
Magnetic ore.. ..	57·01		0·14		0·10		0·07		1

Iron as a silicate is present in most rocks, the oxide of iron imparting the red color to the soil. It is an essential constituent of chlorophyll (the green coloring matter of leaves) and of hæmoglobin (the red coloring matter of blood).

Preparation.—In England iron is usually manufactured from clay iron-stone.

(*a.*) The broken ore is first *roasted* or *calcined*, either in kilns, like lime-kilns, or in heaps exposed to the open air, whereby water, carbonic anhydride, and some sulphur are driven off, and an impure ferric oxide obtained.

(β.) This calcined ore is now *smelted* in the "*blast furnace.*"

The iron blast furnace is a brick building, some 50 or 60 feet high, closed at the bottom, and open at the top for the reception of the charge. Air is forced in at the bottom of the furnace through the air-pipes or *tuyères*, whereby a high temperature is maintained. At the bottom certain tap-holes are placed, through which the melted iron may be drawn off, as well as other orifices, to allow for the overflow of the slag.

The furnace is charged with layers of calcined iron ore, coke, and limestone, fresh layers being introduced as required.

Principle of the blast furnace.—The *coke* burns at the expense of the oxygen of the air supplied through the air-pipes. The CO_2 thus formed passes over the hot fuel, and taking up more carbon becomes CO. This carbonic oxide, coming into contact with the red-hot oxide of iron, becomes oxidized at the expense of the oxygen of the iron oxide, leaving the iron in a metallic state (*zone of reduction*). The heated iron, as it sinks in the furnace, combines with a little carbon, and so forms fusible "*cast iron*" (*zone of carburation*), which, in the hottest part of the furnace (*zone of fusion*), reduces the silica and the phosphates, the iron combining with the free silicon and phosphorus.

The *limestone* ($CaCO_3$), when heated, parts with its CO_2, leaving lime (CaO). This combines with the infusible clay (silicate of alumina) and other impurities in the melted iron, to form a readily fusible double silicate of lime and alumina, which, owing to its less gravity, floats on the surface of the melted iron, and constitutes, when cold, what is termed "*iron slag.*" [This limestone is called "*a flux*" because it makes the clay flow (*fluo*).]

Thus the melted metal, with the fused slag swimming on its surface, collects on the hearth of the furnace. The *slag* is allowed to run from openings in the *upper* part of the hearth, whilst the *metal* is draw off from below into sand channels, each channel of iron being called "*a pig*" ("pig-iron"). The iron thus obtained is known as "cast-iron."

The gas issuing from the chimney of the furnace is highly inflammable and poisonous. The following represents its average percentage composition :—

Nitrogen	55·35	vols.	
Carbonic oxide ...	25·97	,,	
Hydrogen	6·73	,,	
Carbonic acid	7·77	,,	
Marsh gas	3·75	,,	
Olefiant gas	0·43	,,	= 100·00 vols.

The air, previously to its being supplied to the furnace through the "tuyères," is usually heated to 600° F. (315·5° C.) by the furnace gas. This constitutes what is called the "hot blast." In this way a great loss of heat is prevented. It is stated, however, that "*hot blast iron*" is of inferior quality to "*cold blast iron*," hot blast iron both receiving and retaining a larger quantity of impurities.

Cast iron (pig iron) contains about 2 to 5 per cent. of carbon, but it is not a pure carbide such as would be represented by the formula Fe_4C.

Composition of Cast Iron (Percy).

	Maximum.	Minimum.
Carbon	4·81	1·04 per cent.
Silicon	4·77	0·08 ,,
Sulphur	1·06	0·00 ,,
Phosphorus	1·87	trace ,,
Manganese	6·08	trace ,,
Iron	81·41	98·88 ,,

There are several varieties of cast iron known in commerce. In *white iron* (the color of which is due to manganese), the carbon exists in chemical combination with the metal (Sp. gr. 7·53). *Spiegeleisen* (specular pig iron) is white iron containing the highest percentage (6 per cent.) of combined carbon. In *grey iron*, a portion of the carbon is present in an uncombined state (Sp. gr. 6·92). *Mottled iron* is an intermediate variety between white and grey iron. *Cast iron* fuses at about 3000° F. (1648·8° C.). It is hard, non-elastic, and brittle. It cannot be welded.

Wrought iron.—Cast iron is changed into wrought iron by the processes of "*refining*" and "*puddling*." It contains from 0·15 to 0·5 per cent. of carbon.

Refining is for the purpose of effecting the removal from the iron of the carbon, silicon, sulphur, and phosphorus. The melted metal is subjected to the action of a current of air, whereby the silicon and a part of the carbon become oxidised. The silica thus formed unites with the oxide of iron produced simultaneously, to form a fusible slag.

Puddling.—The puddling furnace is a reverberatory furnace; its use is rendered necessary by the circumstance that the metal becomes less fusible as it approaches purity. The fused metal is well *stirred* or "*puddled*," so that the oxidation of the impurities may be effected by their actual contact with oxide of iron. The metal is then well hammered, in order to squeeze out the liquid slag. This hammered mass constitutes ***wrought iron.***

The "Bessemer process" was invented to save the great manual labor involved in ordinary puddling operations. It consists in burning out the carbon and silicon with an air blast ("*converters*"), and then supplying the necessary amount of carbon by the addition of sufficient cast iron (spiegel-eisen) of known composition to convert the whole into steel.

Wrought iron is soft, elastic, malleable and ductile. It is very difficult to melt, but is capable of being welded. It is magnetic.

Steel is prepared by imbedding bars of wrought iron in charcoal and heating them for several days at 2000° F. (1093·3° C.) (Cementation). From the *fibrous* structure peculiar to wrought iron, the metal gradually assumes the *granular* structure of steel. This change is due to the iron throughout the mass combining with about 1 per cent. (from 0·6 to 2·0 per cent.) of carbon. The transference of this carbon is believed to be effected by the formation in the first instance of carbonic oxide, half of the carbon of which is taken up by the iron ($2CO = CO_2 + C$), the CO_2 formed becoming again converted into CO by combining with more carbon. Graham has shown that iron has the power of absorbing or "occluding" six or eight times its volume of carbonic oxide.

The unevenness of the *blistered steel* thus formed is remedied by hammering, whereby *shear steel* is produced. When this is heated to redness, and suddenly cooled by dipping into water or oil, the steel is rendered very hard, brittle and elastic, its volume being slightly increased. By a process of tempering (that is, re-heating and cooling), the steel is prepared for the various purposes for which it may be required, the temper of the metal depending on the temperature at which it is dipped, and the rapidity with which it is cooled. Heated to 430° F. (221° C.), and cooled slowly (called *tempering to the yellow*), the steel becomes very hard, such as is required for knives, etc.; but if heated to 550° F. (287·8° C.) and then cooled (called *tempering to the blue*), it becomes highly elastic, a condition required for watch-springs, etc.

Case hardening, i.e., the conversion of the surface of soft iron articles into steel, is effected by first heating them in contact with bone-dust or other substance containing carbon, and afterwards cooling the metal by dipping it into water.

Steel, unlike iron, retains magnetism. Hence it is used in the manufacture of permanent magnets. A steel blade may be known from an iron blade by placing upon it a drop of dilute nitric acid. A dark stain, from the separation of carbon, will be produced on the face of the blade if made of steel, whilst a green stain will result in the case of the iron blade.

Impurities.—These are *carbon* (0·2 to 0·5 per cent.) (the presence of which increases the hardness of the iron), *silicon, sulphur, phosphorus* and *arsenic.* The iron is injuriously affected by the presence of the last four bodies.

Properties.—(*a.*) *Physical. Pure iron* is soft, of a silvery white color, and takes a high polish. *Bar* iron is a hard, grey, lustrous metal. Iron has no smell unless it be rubbed. Its texture is fibrous. Its specific gravity is about 7·7. When heated it first becomes pasty, and in this condition may be welded.* At a high temperature it may be fused. At a red heat it is both ductile and malleable. It expands slightly during the process of cooling. Compared with other metals its tenacity is enormous, but its conductivity for heat and electricity is comparatively small. It is, in common with nickel and cobalt but in a far higher degree than these metals, remarkably magnetic. A red heat, however, destroys its magnetism, although it recovers it again on cooling. Its magnetism, however, is not permanent, unless the iron be combined with *carbon* as in steel, or with *oxygen* as Fe_3O_4, or with *sulphur* as Fe_3S_4 or Fe_7S_8. Combined with oxygen or sulphur in proportions other than these, the metal is not magnetic at all.

(β.) *Chemical. Action of Air and Oxygen.*—Heated in air iron becomes coated with scales of Fe_3O_4 (smithy scales). *Dry* air has very little action on polished iron, but the metal rapidly rusts in *moist* air, forming $2Fe_2O_3,3H_2O$. The presence of carbonic anhydride expedites the rusting process by the formation of a carbonate of iron ($Fe+H_2O+CO_2=FeCO_3+H_2$), which is soluble in water containing CO_2, but is precipitated from solution by the absorption of oxygen ($4FeCO_3+O_2=2Fe_2O_3+4CO_2$). Once started, the rusting process proceeds rapidly, owing to the hygroscopicity of the iron oxide. Rust always contains ammonia, formed by direct union of the nascent hydrogen with atmospheric nitrogen. The contact of a nail with a wet cloth causes a diffused iron-mould stain, due to the formation of the carbonate of iron. Similarly the black streaks produced a short time after iron nails have been driven into an oak fence, are due to the action of the tannic acid of the oak on the solution of the carbonate of iron formed in the manner already indicated. When heated to a high temperature, iron burns in oxygen brilliantly, throwing out numerous scintillations, Fe_3O_4 being formed. It burns in sulphur vapor. It combines with carbon at a high temperature to form a carbide of iron (Fe_4C). In a state of minute subdivision, the metal fires on mere exposure to air.

Chlorine, bromine, and iodine, in the presence of water, combine rapidly with iron at ordinary temperatures.

Action of Water.—Iron is not acted on by water, when the water is free from air, but it is rapidly attacked by common water containing dissolved air, more especially if the water be exposed to air at the time of its contact with the iron. (*For the action, see above.*) The presence of a free alkali, or of an alkaline earth, or of an alkaline carbonate, interferes with this action. At a red heat, iron decomposes water ($4H_2O+3Fe=Fe_3O_4+4H_2$).

---

* In "welding," the two pieces of pasty metal are first covered with sand. This acts as a flux to the oxide, thus enabling two absolutely clean surfaces to be brought into contact. The slag of silica and oxide of iron formed is forced out by the hammering.

Action of Acids.—Hot or cold concentrated sulphuric acid has a slight action on iron, SO_2 being liberated. Dilute sulphuric acid acts rapidly, evolving hydrogen. Ordinary nitric acid acts energetically upon the metal, NO being evolved. If, however, the iron be first dipped in a nitric acid of specific gravity 1·45, which has no action upon it, and then, without being wiped, be placed in *dilute* nitric acid, the latter will be found to have no action on the metal. A similar change in iron may also be effected by touching it, when immersed in a nitric acid of specific gravity 1·35, with a piece of gold or platinum, the previously energetic action of the acid instantly ceasing (*passive iron*). Passive iron does not precipitate copper from its solutions, although a minute scratch will render the iron active in this respect. This passive condition depends on the deposition of a thin film of Fe_3O_4 on the surface of the metal. Hydrochloric acid acts freely on the metal, hydrogen being set free. Carbonic acid, dissolved in water freed from air, also rapidly attacks iron, with the evolution of hydrogen. Thus, in most chalybeate waters the iron exists as a ferrous carbonate dissolved in a water containing CO_2, a deposit of oxide being thrown down when the water is freely exposed to the action of the air.

Compounds of Iron (Fe=56).

	COMPOUNDS.		Common Formula.	Molecular Weight of Anhydrous Salt.	Specific Gravity of Crystals.	Fe per cent.
1	Oxides.	Ferrous oxide	FeO	72		
2		Ferrous hydrate	FeH_2O_2	90		
3		Ferric oxide	FeH_6O_6	160	4.5 to 5·5	70·0
4		Ferric hydrate	$Fe_2H_6O_6$			
5		Magnetic oxide of iron..	Fe_3O_4 or (FeO,Fe_2O_3)	232	5·0	72·41
6		Hydrated magnetic oxide	Fe_3O_4,H_2O	250		
7		Ferric anhydride (hypothetical)	FeO_3			
8		Ferric acid (hypothetical)	H_2FeO_4	122		45·90
9	Chlorides.	Ferrous chloride ..	$FeCl_2$	127	2·528; Crystals, 1·926	44·09
10		Ferric chloride	Fe_2Cl_6	325		34·36
11		(Bromides and Fluorides similar to Chlorides) ..	$FeBr_2$ and Fe_2Br_6 FeF_2 and Fe_2F_6			
12		Ferrous iodide	$FeI_2,4H_2O$	310	2·873	18·06
13		Nitrides of iron	Fe_4N_2	252		
			Fe_3N	182		
14	Sulphides.	Ferrous sulphide	FeS	88	4·8	63·63
15		Ferric disulphide (bisulphide)	FeS_2	120	4·98	46·66
16		Other sulphides	Fe_2S_2 (?)	176		
			Fe_2S_3	208		
			$H_2Fe_2S_4$ (Sulpho-ferric acid hypothetical			
			Fe_3S_4	296		
			Fe_7S_8	648	4·65	
			FeSAs (Mispickel)		6.13	

		COMPOUNDS.	Common Formula.	Molecular Weight of Anhydrous Salt.	Specific Gravity of Crystals.	Fe per cent.
17	Sulphates.	Ferrous sulphate ..	$FeSO_4,7H_2O$	152+126	1·857	
18		Ferric sulphate	$Fe'''_2 3SO_4$	400		28·00
19	Nitrates.	Ferrous nitrate	$Fe2NO_3,6H_2O$	180+108		31·11
20		Ferric nitrate	$Fe'''_2 6NO_3$	484		
21		Ferrous carbonate	$FeCO_3$	116	3·8	
22		Ferrous phosphate.. ..	$Fe_3P_2O_8 8H_2O$			
23		Ferric phosphate	$FePO_4,2H_2O$	302		37·08
24		Ferrous oxalate	$2FeC_2O_4,3H_2O$	144		38·88
25		Ferrous silicate	Fe_2SiO_4			
26		Iron alum	$K_2SO_4Fe_2 3SO_4,24H_9O$			

Compounds of Iron with Oxygen.

1.	Ferrous oxide	FeO.
2.	Ferrous hydrate	FeH_2O_2.
3.	Ferric oxide	Fe_2O_3.
4.	Ferric hydrate	$Fe_2H_6O_6$.
5.	Magnetic or black oxide of iron ...	Fe_3O_4.
6.	Hydrated magnetic oxide	Fe_3O_4, H_2O.
7.	Ferric anhydride	FeO_3.
8.	Ferric acid	H_2FeO_4.

(1, 2.) **Ferrous Oxide**.—*Protoxide of iron* (FeO). This body is almost unknown in the free state.

Preparation.—(1.) (*Anhydrous.*) By heating Fe_2O_3 to redness in a current of hydrogen. (2.) (*As a hydrate,* FeH_2O_2, *hydrated protoxide of iron.*) By precipitating a solution of a ferrous salt with an alkali, care being taken that the water in which the ferrous salt is dissolved is entirely free from air.

Properties.—FeO is a black and spontaneously inflammable powder. By combustion it yields Fe_2O_3. The white hydrated ferrous oxide rapidly absorbs oxygen from the air, becoming the hydrate of ferric oxide ($Fe_2O_3,3H_2O$). It is a powerful base, forming *ferrous salts* (*protosalts of iron*), in which the iron is bivalent. These salts are of a green color, and rapidly oxidize when exposed to the air. The oxide is used to stain glass a green color. It absorbs CO_2, heat being produced during combination. Soluble in 150,000 of water, the solution being alkaline.

(3, 4.) **Ferric Oxide** (Fe_2O_3).

Synonyms.—*Red oxide: Sesquioxide* or *peroxide of iron; colcothar; jewellers' rouge;* (obtained as a bye-product in the production of fuming sulphuric acid); *Venetian red; crocus of Mars*, etc.

History.—It is found native as *hæmatite, specular iron ore, bloodstone*, etc.

Preparation.—(1.) (*Anhydrous.*) By the ignition of ferrous sulphate ($2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$).

(2.) (*As a hydrate*, $Fe_2O_3,3H_2O = Fe_2H_6O_6$, *iron rust.*) By acting on a solution of ferric chloride with an excess of ammonia.

Properties.—Ferric oxide is a dark red powder, insoluble in water, although what is called "dialysed iron" (formed by dissolving ferric hydrate in ferric chloride and dialysing), is practically ferric oxide dissolved in water. In this condition, however, it undergoes rapid conversion into ferric hydrate and water. The hydrate is soluble in acids. When air-dried, it undergoes partial dehydration. Heated to 608° F. (320° C.) it forms Fe_2O_3. If in this condition it be heated to redness, it exhibits a sudden glow, and contracts in bulk, and, notwithstanding that its composition remains unaltered (the change being molecular), it will be found to have become insoluble in acids. By heating to whiteness oxygen is evolved, and a magnetic oxide formed ($3Fe_2O_3 = 2Fe_3O_4 + O$). With acids it forms *ferric salts* (*persalts of iron*), in each molecule of which are two atoms of triad iron. Ferric salts are non-crystalline and deliquescent, of a reddish colour, having an astringent taste and an acid reaction.

Like alumina, with which it is isomorphous, it can, although in a lesser degree, act the part of a feeble acid to strong bases, as *e.g.*, in the compound $4CaO,Fe_2O_3$.

Uses.—Ferric oxide is found in all soils. It serves as a carrier of air to organic matter, whereby CO_2 is prepared for the plant. The ferrous oxide thus formed is again oxidized to ferric oxide, and so fitted once more to perform the same process. The hydrated ferric oxide is largely used as a material for purifying coal-gas from sulphuretted hydrogen ($(Fe_2O_3,H_2O) + 3H_2S = (Fe_2S_3,H_2O) + 3H_2O$). The hydrated ferric sulphide formed is oxidized ("revivified") by exposure to air, considerable heat accompanying the process ($2(Fe_2S_3,H_2O) + 3O_2 = 2(Fe_2O_3,H_2O) + 3S_2$). The ferric oxide thus reproduced may be employed again and again until the free sulphur formed has accumulated in such quantity that it impairs the power of the oxide to absorb the gas.

(5, 6.) **Magnetic Oxide of Iron.**—*Black oxide*; *ferroso-ferric oxide* (Fe_3O_4 or FeO,Fe_2O_3). The latter formula for this compound is believed to be the correct one, minerals being known having the same crystalline form, where the iron is displaced by other metals, *e.g.*, spinelle (MgO,Al_2O_3). It occurs native as *loadstone, magnetite*, etc., and is the chief constituent of the black scales falling from the anvil during the working of wrought iron.

Preparation.—(1.) (*Anhydrous.*) (α.) By burning iron in oxygen (*smithy scales*). (β.) By passing steam or CO_2 over hot iron filings (H or

CO being liberated). (γ.) By boiling freshly precipitated hydrated ferric oxide in water, together with an excess of iron turnings.

(2.) (As *a hydrate. Hydrated magnetic oxide; ferroso-ferric hydrate;* Fe_3O_4, H_2O). By adding ammonia to a mixed solution of equivalent parts of ferrous and ferric sulphates, and boiling.

Properties.—The black oxide is fusible at high temperatures. It is soluble in nitric and in hydrochloric acids. It does not form definite compounds with acids, but simply mixtures of ferrous and ferric salts.

(7, 8.) Ferric Acid (H_2FeO_4).—The Ferrates.

Neither ferric anhydride nor ferric acid have been prepared, being only known in combination as ferrates. A *potassium ferrate* solution (K_2FeO_4) may be prepared either by dissolving an ignited mixture of ferric oxide and nitre in water, or by passing chlorine through a solution of potash (30 parts of KHO in 50 parts of H_2O) in which one part of freshly-precipitated hydrated ferric oxide is suspended ($Fe_2O_3,3H_2O + 3Cl_2 + 10KHO = 6KCl + 2K_2FeO_4 + 8H_2O$). This potassium salt is very soluble in water, but insoluble in a strong potash solution. Its aqueous solution has a fine purple color. It rapidly decomposes ($2K_2FeO_4 = 2K_2O + Fe_2O_3 + 3O$), oxygen being evolved and ferric oxide precipitated. The presence of organic matter, or the application of heat, or the addition of an acid decomposes it immediately.

A sodium ferrate (Na_2FeO_4) and a barium ferrate ($BaFeO_4$) have been prepared.

COMPOUNDS OF IRON AND CHLORINE.

9. Ferrous chloride	$FeCl_2$.
10. Ferric chloride	Fe_2Cl_6.

(9.) Ferrous Chloride, *Protochloride of Iron* ($FeCl_2$).

Preparation.—(1.) (*Anhydrous.*) (α.) By passing dry hydrochloric acid gas over red-hot iron ($Fe + 2HCl = FeCl_2 + H_2$).

(β.) By heating ferric chloride in hydrogen ($Fe_2Cl_6 + H_2 = 2FeCl_2 + 2HCl$).

(2.) (As a *hydrate;* crystals $= FeCl_2, 4H_2O$.) By dissolving iron in hydrochloric acid, and evaporating with exclusion of air.

Properties.—The crystals are six-sided and deliquescent, of a green color, and very soluble in water and in alcohol. The salt rapidly oxidizes, even by mere exposure to air. When heated in air, it is decomposed ($6FeCl_2 + 3O = Fe_2Cl_6 + Fe_2O_3$). The solution rapidly dissolves nitric oxide.

(10.) Ferric Chloride; *Perchloride; Sesquichloride* (Fe_2Cl_6).

Preparation.—(1.) (*Anhydrous,* Fe_2Cl_6.) (α.) By passing a current of chlorine over red-hot iron. (β.) By heating ferrous chloride in chlorine.

(2.) (As a *hydrate,* $Fe_2Cl_6,6H_2O$.) (α.) By dissolving ferric oxide in hydrochloric acid, or the metal in aqua regia.

(β.) By passing chlorine through a solution of ferrous chloride.

Properties.—The *anhydrous* chloride is very deliquescent. It fuses and is volatile. It absorbs ammonia, forming ($Fe_2Cl_6,2NH_3$). It dissolves in alcohol and ether, and rapidly combines with water, forming a red solution. Heated with oxygen, it yields chlorine and ferric oxide, and with steam, ferric oxide and hydrochloric acid. The *hydrate* is a *red* crystalline body, decomposed by heat into Fe_2O_3 (or perhaps an oxychloride) and HCl. Hence the anhydrous chloride cannot be prepared from the hydrate. It forms double salts with alkaline chlorides, such as the garnet-like crystals of $Fe_2Cl_6,4KCl,2H_2O$.

Uses.—In solution it is used as a disinfectant, on account of the ease with which it yields chlorine to organic matter, itself being reduced to ferrous chloride. It is used in *medicine* and in the *laboratory*. Its solution freely dissolves freshly precipitated ferric hydrate, forming ferric oxychloride.

Ferric Bromide and **Fluoride** have been prepared. **Ferric Iodide** has not been prepared.

(11.) **Ferrous Bromide** ($FeBr_2$) is formed when bromine vapour is passed over red hot iron filings. **Ferrous Fluoride** (FeF_2) may be prepared by dissolving iron in hydrofluoric acid.

(12.) **Ferrous Iodide** (FeI_2).

Preparation.—By digesting iron and iodine in water.

Properties.—It decomposes by exposure to air. Hence it is commonly prescribed in medicine in the form of a syrup, by which means its oxidation is retarded.

(14.) **Ferrous Sulphide**; *Protosulphide* or *Sulphide of Iron* (FeS).

Preparation.—(1.) (*Anhydrous.*) By direct union of sulphur with iron at a high temperature.

(2.) (As a *hydrate.*) By precipitating a ferrous salt with an alkaline sulph-hydrate ($2KHS + FeSO_4 + H_2O = FeS,H_2O + H_2S + K_2SO_4$).

Properties.—The anhydrous sulphide is insoluble in water and in alkalies, but is soluble in dilute sulphuric and hydrochloric acids, H_2S being evolved. Heated *in vacuo*, no sulphur is evolved even at a white heat. When heated in the air it first becomes $FeSO_4$, this compound being itself decomposed at a higher temperature, yielding a residue of Fe_2O_3. The hydrate rapidly absorbs oxygen when exposed to the air, forming the red ferric oxide and free sulphur.

(15.) **Ferric Disulphide** (FeS_2) is found native in all rocks as *iron pyrites* (*mundic*), and is probably formed by the deoxidation of ferrous sulphate by organic matter. Specific gravity, 5·185. A white iron pyrites (*marcasite*) is also found in nature.

Preparation.—By heating iron with excess of sulphur at a temperature below redness.

Properties.—By exposure to air some varieties (such as *marcasite*, Specific gravity, 4·8) rapidly absorb oxygen, forming ferrous sulphate. Ferric disulphide is a hard body not attracted by the magnet. It is not acted on either by cold sulphuric or hydrochloric acids. Hot sulphuric acid dissolves it with evolution of SO_2; hot nitric acid oxidizes and slowly dissolves it. By the action of heat upon it sulphur is driven off, and Fe_3S_4 formed. On account of this property, iron pyrites is largely used in the manufacture of sulphuric acid. (*See* page 181.)

(16.) **Ferric Sulphide** (Fe_2S_3) is formed by heating iron with its own weight of sulphur.

Certain salts have been prepared, called *sulpho-ferrites,* of which $K_2Fe_2S_4$ is an example.

The sulphide Fe_7S_8 occurs native as *magnetic pyrites.*

Iron Oxy-Salts.

(17.) **Ferrous Sulphate**—*Protosulphate of iron; copperas; green vitriol; iron vitriol* ($FeSO_4$).

Preparation.—(1.) By acting on iron with dilute sulphuric acid and crystallizing ($FeSO_4,7H_2O$). [Other hydrates of $FeSO_4$ have also been obtained.]

(2.) By the oxidation of iron pyrites (FeS_2) by exposure to air and moisture. (*See above.*)

(3.) By the action of a copper sulphate solution on scrap iron.

Properties.—A green, dimorphous (rhomboids and oblique prisms), efflorescent salt ($FeSO_4,7H_2O$), soluble in alcohol and in water (1 in 2 aq. at 60° F.; 3·7 in 1 aq. at 194° F.; 3·3 in 1 aq. at 212° F.). At 212° F. (100° C.) $FeSO_4,7H_2O$ becomes $FeSO_4,H_2O$. At 500° F. (260° C.) it becomes $FeSO_4$. At a red heat the salt undergoes decomposition ($2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$). The preparation of *Nordhausen sulphuric acid* from ferrous sulphate, depends on the circumstance that it is practically impossible to render the sulphate in large bulk perfectly anhydrous, and that therefore the little water remaining in the salt distils over along with the SO_3. The residue (Fe_2O_3) left in the retort when the process is complete is called *colcothar.*

By exposing a solution of the salt to air, a brown liquid results, due to the formation of a normal and a basic ferric sulphate, the former remaining in solution, whilst the latter is precipitated ($10FeSO_4 + O_5 = 3(Fe_2O_3,3SO_3) + 2Fe_2O_3,SO_3$). A similar result occurs by the exposure of the solid crystals to air, especially if the air be moist. The aqueous solution of the salt rapidly absorbs nitric oxide. It forms double salts with alkaline sulphates, isomorphous with their compounds with magnesium salts ($(NH_4)_2Fe2SO_46H_2O$).

Uses.—In the *laboratory,* as a reducing agent, *e. g.*, to precipitate metallic gold from its solutions. In *the arts,* in the manufacture of black dyes, ink, &c., by the action of tannic acid upon it.

(18.) **Ferric Sulphate.** — *Persulphate* or *sesquisulphate of iron* ($Fe'''_2 3SO_4$), is found native in Chili, as *coquimbite* ($Fe_2 3SO_4,9H_2O$).

Preparation.—[Several sulphates of ferric oxide are known.] By adding the necessary quantity of H_2SO_4 to $Fe''SO_4$ to convert it into $Fe_2 3SO_4$. The mixture is then boiled, the iron being afterwards peroxided by the cautious addition of nitric acid, until no blue precipitate is produced with potassic ferricyanide ($6FeSO_4+3H_2SO_4+2HNO_3=3Fe_2 3SO_4+2NO+4H_2O$).

Properties.—A non-crystalline, yellow body, soluble in water.

If potassium sulphate be dissolved in proper proportion in a solution of ferric sulphate, and kept at a low temperature, *iron alum* crystallizes out ($K_2SO_4,Fe_2 3SO_4,24H_2O$).

(19.) **Ferrous Nitrate** ($Fe2NO_3,6H_2O$).

Preparation.—By the action of cold dilute nitric acid on ferrous sulphide, or by decomposing ferrous sulphate with barium nitrate.

(20.) **Ferric Nitrate** ($Fe'''_2 6NO_3,12H_2O$).—Prepared by the action of nitric acid of specific gravity 1·2 on metallic iron.

[N.B.—Fuming nitric acid (specific gravity 1·5) has no action on iron. (*See* Passive Iron, p. 404.)

(21.) **Ferrous Carbonate,** *Protocarbonate of iron* ($FeCO_3$), is found native as *spathic iron ore*, and as *clay iron ore.* It is the iron salt commonly found in mineral waters, retained in solution by the carbonic acid dissolved in the water, from which the iron may be precipitated by the action of oxygen, as a red rusty deposit of ferric hydrate. This deposit is frequently seen on the ground in the neighbourhood of chalybeate springs.

Preparation.—By mixing together solutions of an alkaline carbonate and a ferrous salt.

Properties.—The hydrate formed as above is first white, but afterwards dark-colored, evolving CO_2 and absorbing O (becoming $Fe_2H_6O_6$) by mere exposure to air.

(24.) **The Iron Oxalates** are found native (*Humboldtite* or *iron-resin*), and may be prepared as lemon-yellow precipitates, by the action of ferrous sulphate upon ammonic oxalate.

Ferrous and ferric phosphates, and ferrous and ferric silicates (refinery slag) have been prepared.

Reactions of Iron Compounds.

Non-luminous flame—No action.

Spark spectrum—Innumerable lines.

Heated with sodium carbonate on charcoal, a black magnetic powder is left.

Borax bead—Green in reducing flame ; no color in oxidizing flame.

(1.) Ferrous Salts.

Caustic Alkalies—White ppt. (FeH_2O_2) which changes green on exposure.

Ammonia—Partial precipitation of FeH_2O_2.

Sulphuretted hydrogen—No ppt. in acid solution.

Ammonium Sulphide—Black ppt. (FeS,H_2O), oxidized by exposure.

Potassium Ferrocyanide—White ppt. (ferrous ferrocyanide), becoming blue by exposure.

Potassium Ferricyanide—Deep blue ppt. (ferrous ferricyanide or Turnbull's blue).

(2.) Ferric Salts.

Caustic Alkalies and Ammonia—A reddish ppt. ($Fe_2H_6O_6$) insoluble in excess.

Sulphuretted Hydrogen—Ppt. of white sulphur. [Ferric reduced to ferrous condition.]

Ammonium Sulphide—A black ppt. (FeS,H_2O), with separation of sulphur.

Potassium Ferrocyanide—A deep blue ppt. (Prussian blue).

Potassium Ferricyanide—No ppt. Solution becomes of a reddish-brown color.

Ammonium Sulphocyanide—Blood-red color; permanent with hydrochloric acid.

Barium Carbonate—Ppt. of $Fe_2H_6O_6$ with evolution of CO_2.

CHROMIUM (Cr).

Atomic weight, 52·1. *Specific gravity*, 7·31. *Atomicity*; *dyad, tetrad, and hexad, also a pseudo-triad and octad* (CrO; CrO_3).

History.—Obtained by Vauquelin (1797), from lead chromate. Termed chromium (χρῶμα, color) from the varied colors of its compounds.

Natural History.—It does not occur free, but is found as *chrome iron-slate* or *chrome iron-stone* (FeO,Cr_2O_3), as lead-chromate ($PbCrO_4$), etc.

Preparation.—(1.) By reducing chromic oxide with charcoal.

(2.) By the action of sodium or potassium on chromic chloride.

(3.) By heating a mixture of zinc and chromic chloride to about 1,000° C. (using KCl and NaCl as a flux). If after the action is complete, the zinc be dissolved out of the residue with warm dilute nitric acid, metallic chromium will be found undissolved in the form of a grey crystalline powder (Wöhler).

(4.) By the electrolysis of a solution of chromous and chromic chlorides (Bunsen).

Properties.—(*α.*) *Physical.* A hard, crystalline (octahedra), highly infusible metal.

(*β.*) *Chemical.* It is not readily oxidized by heating in a Bunsen, but burns in the oxyhydrogen flame. It is soluble in HCl and in hot H_2SO_4, hydrogen being evolved in both cases. Neither cold dilute sulphuric acid nor boiling HNO_3 have any action upon it. It is converted into a chromate by ignition with the hydrated alkalies.

It hardens steel even when present to the extent of 0·5 per cent.

Compounds of Chromium (Cr = 52).

	COMPOUNDS.	Formula (Common).	Molecular Weight.	Specific Gravity.	Cr per cent.
1	Chromous oxide (?)	CrO	68·0		76·47
2	,, hydrate	CrH_2O_2			
3	Chromic oxide	Cr_2O_3	152·0	5·21	68·42
4	,, hydrate	$Cr_2H_6O_6$			
5	Trichromic tetroxide	Cr_3O_4			
6	Chromic peroxide	CrO_2			
7	,, anhydride	CrO_3	100·0	2·676	52·00
8	,, acid	H_2CrO_4			
9	Perchromic acid	$H_2Cr_2O_8$ (?)			
10	Potassium chromate	K_2CrO_4	194·2	2·682	26·77
11	,, bichromate	$K_2O(CrO_3)_2$	294·2	2·624	35·35
12	,, trichromate	$K_2O(CrO_3)_3$	394·2		39·57
13	,, tetrachromate	$K_2O(CrO_3)_4$	494·2		42·08
14	Sodium chromate	Na_2CrO_4	162·0		32·09
15	,, dichromate	$Na_2O(CrO_3)_2$			
16	Ammonium chromate	$(NH_4)_2CrO_4$			
17	,, dichromate	$(NH_4)_2O(CrO_3)_2$			
18	Barium chromate	$BaCrO_4$	253·0		20·55
19	,, dichromate (yellow ultramarine)	$BaO(CrO_3)_2\ 2H_2O$,			
20	Strontium chromate	$SrCrO_4$			
21	Calcium chromate	$CaCrO_4,2H_2O$			
22	Magnesium chromate	$MgCrO_4,7H_2O$			
23	Potassium magnesic chromate	$K_2CrO_4,MgCrO_4\ 2H_2O$			
24	Plumbic chromate	$PbCrO_4$	323·0	5·653	16·09
25	,, ,, (basic)	$2PbO,CrO_3$		6·266	
26	Argentic chromate	Ag_2CrO_4	332·0	5·77	23·21
27	Mercuric ,,	$HgCrO_4$			
28	Chromous chloride, etc.	$CrCl_2$; $CrBr_2$	123·0		42·27
29	Chromic chloride, etc.	Cr_2Cl_6; Cr_2Br_6; Cr_2F_6	317·0		32·80
30	,, perfluoride	CrF_6			
31	,, oxychloride	$CrCl_2O_2$	155·0	1·92	33·54
32	,, oxychlorhydrate (chloro-chromic acid)	CrO_3,HCl (?)			
33	,, sulphide	Cr_2S_3	200·0		52·00
34	,, nitride	CrN			
35	Chromous sulphate	$Cr''SO_4$			
36	,, potassic sulphate	$Cr''K_2 2SO_4$			
37	,, phosphate	$Cr_3P_2O_8$			
38	,, carbonate	$Cr''CO_3$			
39	Chromic nitrate	$Cr_2 6NO_3$			
40	,, sulphate	$Cr_2 3SO_4,15H_2O$	392+270		26·53
41	,, potassium sulphate (chrome alum)	$Cr_2K_2 4SO_4,24H_2O$			

Compounds of Chromium and Oxygen, Etc.

1.	Chromous oxide	CrO (?),
2.	„ hydrate	CrH_2O_2
3.	Chromic oxide	Cr_2O_3.
4.	„ hydrate	$Cr_2H_6O_6$.
5.	Trichromic tetroxide	Cr_3O_4.
6.	Chromic peroxide	CrO_2.
7.	„ anhyhride	CrO_3.
8.	„ acid	H_2CrO_4.
9.	„ perchromic acid	$H_2Cr_2O_8$.

(1, 2.) **Chromous Oxide** (CrO) (*Chromous monoxide*) is only known as a *hydrate* (CrH_2O_2). This is produced as a brown precipitate on adding potassium hydrate to a solution of chromous chloride. The moist precipitate absorbs oxygen with great energy, forming (CrO, Cr_2O_3). Heated without air it forms Cr_2O_3, evolving hydrogen and water. It is a feeble base, somewhat insoluble in acids.

(3, 4.) **Chromic Oxide.**—*Sesquioxide of chromium* (Cr_2O_3).

Natural History.—Occurs native as chrome ochre.

Preparation.—(1.) (*Anhydrous.*) (*a.*) By heating a mixture of sulphur and potassium bichromate. The Cr_2O_3 remains undissolved when the mass is treated with water. (β.) By the action of heat on chromic hydrate, or on ammonium bichromate, or on a mixture of potassium bichromate with ammonium chloride.

(2.) By passing the vapor of chromic oxychloride (CrO_2Cl_2) through a red-hot pipe.

(3.) (*As a hydrate*, $Cr_2H_6O_6$.) If a solution of potassium bichromate acidulated with sulphuric acid, be boiled with alcohol, or if a current of SO_2 be passed through a solution of the bichromate, a chromic sulphate is formed. On adding ammonia to this solution, or to any chromic salt free from alkali, the hydrate $Cr_2O_3,7H_2O$, of a pale blue color, is precipitated. This may be dried in a current of hydrogen until it becomes a hydrate of the composition Cr_2O_3,H_2O. On ignition, it leaves Cr_2O_3.

Properties.—Chromic oxide is insoluble in acids. It has a brilliant green color, unaffected by heat, a property rendering it valuable in enamel painting (chrome green). When ignited it may be obtained in the form of black hexagonal crystals. It constitutes the green coloring matter of the emerald.

Chromic oxide unites with basic oxides to form a class of compounds that may be regarded as *chromites*, or salts of chromous acid $H_2Cr_2O_4$ (*e.g.* $Zn''Cr_2O_4(=ZnO,Cr_2O_3)$; $MnCr_2O_4$; $FeCr_2O_4$).

Chromic hydrate when freshly precipitated dissolves in ammonia, the solution being peach-colored (chrom-amine). A colloidal form results when the precipitate is dissolved in a solution of chromic chloride and dialysed. The hydrate forms two sets of salts with acids, one of which is green and non-crystalline, and the other violet and crystalline. "*Guignet's green*" has the composition $Cr_2O_3,2H_2O$.

(5.) Trichromic Tetroxide (Cr_3O_4).

Preparation.—(1.) (*Anhydrous.*) By the decomposition of an aqueous solution of chromous chloride by a weak electric current.

(2.) (*As a hydrate.*) By adding potassium hydrate to a solution of chromous chloride with *partial* access of air.

Properties.—The oxide readily absorbs oxygen, becoming Cr_2O_3. The hydrate is a reddish brown precipitate.

(6.) Chromic Peroxide (*Chromyl*, CrO_2). Prepared by the reduction of chromic acid. A brown powder.

(7.) Chromic Anhydride (Chromic acid) (CrO_3).

Preparation.—By adding an excess of sulphuric acid to a strong solution of potassium bichromate, and crystallizing.

Properties.—Chromic anhydride crystallizes in needle-shaped crystals, which are deliquescent and very soluble in water, yielding a red solution. It is decomposed at 482° F. (250° C.) with the evolution of oxygen and the formation of Cr_2O_3. It is a powerful oxidizing body ($4CrO_3 = 2Cr_2O_3 + 3O_2$), SO_2,H_2S, and most organic bodies, effecting its reduction. It is employed as an agent in bleaching certain oils. Heated with hydrochloric acid, chlorine is liberated, and Cr_2Cl_6 formed. It is soluble in strong and in dilute sulphuric acid, oxygen being set free on the addition of the strong acid. It is almost insoluble, however, in a sulphuric acid containing 16 to 17 per cent. of water. It is soluble without decomposition in glacial acetic acid. The color of the ruby is believed to be due to the presence of a trace of chromic anhydride.

(8.) Chromic Acid (H_2CrO_4 *hypothetical*).—The Chromates.

Chromic acid, H_2CrO_4, has not been prepared. When separation of the acid is attempted, it at once breaks up into water and CrO_3. It is dibasic (like H_2SO_4), but differs from other dibasic acids in not producing acid salts (*e.g.*, no hydric potassic chromate is known). Such compound (if formed at all) at once becomes a bichromate by a combination of two molecules of the salt, and the elimination therefrom of one molecule of water. Thus :—

$$\underset{\substack{\text{Potassium hydric chromate}\\ \text{(hypothetical)}}}{2KHCrO_4} = \underset{\text{Potassium bichromate}}{K_2O(CrO_3)_2} + \underset{\text{Water.}}{H_2O.}$$

On the addition of a base to a solution of bichromate, it is at once converted into a normal chromate :—

$$K_2O(CrO_3)_2 + 2KHO = 2K_2CrO_4 + H_2O.$$

A somewhat similar relationship to that subsisting between chromic and dichromic acids, exists in the case of sulphuric and disulphuric acids (p. 183), and of phosphoric and pyrophosphoric acids (p. 162).

(9.) **Perchromic Acid** ($H_2Cr_2O_8$).—This compound is supposed to be formed by the action of peroxide of hydrogen on chromic anhydride or on a chromate acidulated with H_2SO_4. The blue color produced by these reactions is supposed to be perchromic acid. This blue color is soluble in ether. When, however, the ethereal solution is evaporated to dryness, CrO_2 only remains.

The reaction forms a delicate test for peroxide of hydrogen (p. 250).

(10.) Potassium Chromate (K_2CrO_4).

Preparation.—(1.) By adding potassic hydrate or carbonate to a solution of potassium bichromate.

(2.) By fusing a chromium compound with nitre or with potassium carbonate in the presence of air.

(3.) *See Potassium Bichromate* (below).

Properties.—A yellow crystalline salt, isomorphous with potassium sulphate. It is soluble in water (1 in 2 aq. at 60° F.), the solution having an alkaline reaction. Its solution is decomposed by CO_2, a bichromate being formed. It fuses without decomposition by heat, changing from a yellow to a red color (Sp. gr. 2·7).

(11.) Potassium Bichromate, $K_2O(CrO_3)_2$, or $K_2Cr_2O_7$.

Preparation.—(1.) By the action of sulphuric acid on potassium chromate.

(2.) Commercially the salt is prepared as follows:—Powdered chrome ironstone is roasted, ground, and mixed with chalk or lime and potassium carbonate (crude potash). The mixture is then heated to bright redness in the oxidizing flame of the reverberatory furnace. The ferrous oxide is thus changed into the insoluble ferric oxide, and the chromic oxide (Cr_2O_3) into chromic acid (CrO_3) which, with the potash, forms potassic chromate (K_2CrO_4). The mass is then acted on with a minimum of boiling water, and the clear solution mixed either with sulphuric acid (in quantity equal to one-half the potassium present) or with nitric acid, and crystallized:—

(α.) $2K_2CrO_4 + 2HNO_3 = K_2Cr_2O_7 + 2KNO_3 + H_2O.$
Potassic chromate + Nitric acid = Potassic bichromate + Potassic nitrate + Water.

(β.) $2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$
Potassic chromate + Sulphuric acid = Potassic bichromate + Potassic sulphate + Water.

Properties.—A red crystalline salt. It fuses at a moderate heat, but is decomposed when the heat approaches redness, with the evolution of oxygen, and the formation of the normal chromate (K_2CrO_4) and Cr_2O_3. It is soluble in water (1 in 10 aq. at 60° F.). Solution acid.

—Treated with H_2SO_4, it gives off oxygen, a solution remaining, which, on standing, yields crystals of "*chrome alum.*" It is used in calico printing as an oxidising agent, etc. (Sp. gr. 2·68.)

Potassium trichromate, $K_2O(CrO_3)_3$, and *tetrachromate*, $K_2O(CrO_3)_4$, have also been prepared.

(24.) **Plumbic Chromate.**—*Chromate of lead; Chrome yellow* ($PbCrO_4$). This body is found native as *red lead ore* (Siberia).

Preparation.—By the action of lead acetate on a solution of potassium chromate.

Properties.—A yellow poisonous pigment. It fuses by heat without decomposing. It effects rapid and complete oxidation of organic matter when heated with it ($8PbCrO_4 = 4(PbCrO_4,PbO) + 2Cr_2O_3 + 3O_2$). It is insoluble in water and in acetic acid, but is soluble in nitric acid and in an excess of potassium hydrate.

Uses.—It is used as a yellow pigment in calico printing, etc. In the *laboratory* it is employed as a source of oxygen in organic combustion analysis, more especially in cases where sulphur is present in the organic compound.

(25.) **Plumbic Chromate (Basic).**—*Orange chrome; chrome red* ($2PbO,CrO_3$, or $PbCrO_4,PbO$).

Preparation.—By boiling together lime and plumbic chromate :—

$$\underset{\text{Plumbic chromate}}{2PbCrO_4} + \underset{\text{Lime}}{CaO} = \underset{\text{Basic plumbic chromate}}{PbCrO_4,PbO} + \underset{\text{Calcium chromate.}}{CaCrO_4.}$$

Properties.—A scarlet pigment. It is used in calico printing, the fabric being first dyed with plumbic chromate, and afterwards boiled in lime-water.

(28.) **Chromous Chloride** ($CrCl_2$).

Preparation.—(1.) By heating chromic chloride in a current of dry hydrogen.

(2.) By dissolving the metal in HCl.

Properties.—A white crystalline substance. The aqueous solution presents a blue color, becoming green by exposure. A powerful reducing agent.

(29.) **Chromic Chloride.**—*Sesquichloride of chromium* (Cr_2Cl_6).

Preparation.—(1.) (*Anhydrous.*) By passing dry chlorine over a heated mixture of chromic oxide and charcoal. The Cr_2Cl_6 collects as a violet sublimate in the cool part of the tube.

(2.) (*As a hydrate.*) (*a.*) By dissolving chromic hydrate in hydrochloric acid ; or (*β*) by boiling either chromic acid, or the lead or silver chromate, with hydrochloric acid and some reducing agent, such as alcohol, SO_2, etc.

Properties.—Heated in air, chromic chloride yields Cr_2O_3 and free chlorine. Insoluble in acids, or in cold or boiling water. If a trace of chromous chloride (or stannous chloride or other reducing agent) be added to the salt suspended in water, a green solution results, great heat being evolved. This solution on evaporation yields crystals of $Cr_2O_6,12H_2O$. This hydrate when heated in air yields the oxychloride (CrO_2Cl_2), but when heated in hydrochloric acid gas gives Cr_2Cl_6.

(30.) **Chromic Perfluoride** (CrF_6). *Preparation.*—By heating calcium fluoride with plumbic chromate and sulphuric acid ($3CaF_2 + PbCrO_4 + 4H_2SO_4 = CrF_6 + PbSO_4 + 3CaSO_4 + 4H_2O$).

A red fuming liquid, decomposed by water.

(31.) **Chromic Oxydichloride** ($CrCl_2O_2$).

Preparation.—By distilling sulphuric acid with a fused mixture of common salt and potassium bichromate;—

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 = K_2SO_4 + 2Na_2SO_4 + 3H_2O + 2CrCl_2O_2.$$

Properties.—A red liquid (Sp. gr. 1·92) emitting suffocating red fumes (Sp. gr. of vapor, 5·52). It catches fire when dropped into alcohol or into a solution of ammonia. It is decomposed by water, yielding chromic and hydrochloric acids. It boils at 244·4° F. (118° C.). It is a powerful oxidizing agent, phosphorus, alcohol, and other oxidizable bodies firing when brought into contact with it.

(32.) **Chromic Oxychlorhydrate.** *Chlorochromic acid* (CrO_3,HCl) is not known in a free state. Certain *chlorochromates* have been prepared [*e.g.*, CrO_3,KCl (potassic chlorochromate), made by gently heating bichromate of potash with hydrochloric acid].

(33.) **Chromic Sulphide** (*sesquisulphide*), (Cr_2S_3) has been obtained by direct union, and also by heating Cr_2O_3 in the vapor of CS_2, or Cr_2Cl_6 in a current of H_2S. Specific gravity, 3·7.—When the sulphide is heated in air, Cr_2O_3 is formed.—It cannot be prepared by a wet process, since it is decomposed by water ($Cr_2S_3 + 6H_2O = Cr_2H_6O_6 + 3H_2S$).

(40.) **Chromic Sulphate** (Cr_23SO_4).—There are three varieties of chromic sulphate:—

(*a.*) A *green* sulphate ($Cr_23SO_4,5H_2O$), which is soluble in alcohol and is non-crystalline. It is prepared either (i.) by boiling hydrated chromic oxide with sulphuric acid, or (ii.) by boiling a solution of the violet sulphate, or (iii.) by heating the crystals of the violet sulphate to 212° F. (100° C.).

(*β.*) A *violet* sulphate ($Cr_23SO_4,15H_2O$), which is insoluble in alcohol and is crystalline. It is prepared by digesting the dried hydrated sesquioxide with sulphuric acid at ordinary temperatures. With potassic sulphate, it forms *chrome alum* ($K_2Cr_24SO_4,24H_2O$, Sp. gr. 1·826), a body crystallising in red octahedra, and used in dyeing, calico printing, and tanning operations.

(γ.) A *red* sulphate (Cr_23SO_4). A crystalline salt, insoluble either in alcohol, water, or acids (even in aqua regia). It is prepared by heating the green or the violet variety to 698° F. (370° C.).

REACTIONS OF CHROMIUM COMPOUNDS.

Non-luminous flame. No action.

Spark spectrum. Bright lines in green and blue.

A. CHROMATES—

Lead acetate ; a yellow ppt. of $PbCrO_4$.

Argentic nitrate ; a red ppt. of Ag_2CrO_4.

Hydrochloric acid (heated) evolves chlorine. Color of salt changes green.

Sulphuretted hydrogen, reduces chromates with separation of sulphur.

B. CHROMIC COMPOUNDS (Solutions violet-colored or green; reaction acid)—

Ammonia ; a pale blue ppt. ($Cr_2H_6O_6$), soluble in excess.

Caustic alkalies; a ppt. ($Cr_2H_6O_6$), soluble in excess ; reprecipitated on boiling.

Sulphuretted hydrogen ; no ppt.

Ammonium sulphide; ppt. of $Cr_2H_6O_6$, with evolution of H_2S.

When a compound of chromium is fused with sodic carbonate and potassic nitrate, a soluble chromate is formed, which when dissolved in water, yields a yellow solution.

ZINC (Zn'').

Atomic and Molecular weight, 65·3 (*see* page 39). *Specific gravity,* 6·8 to 7·2. *Atomicity, dyad* ($''$) [ZnO ; $ZnCl_2$]. *Fuses at* 773° F. (412° C.); *boils at* 1904° F. (1040° C.); *volatilizes at a red heat. Specific heat,* 0·095.

History.—It was known as "Spelter" in the thirteenth century but was not recognised as a distinct metal until the sixteenth. The metal was described by Paracelsus.

Natural History.—Zinc has been stated to have been found in a free state in Melbourne, but of this there is some doubt. It occurs as a *carbonate* ($ZnCO_3$) in calamine, as a *sulphide* (ZnS) in blende, as an *oxide* (ZnO associated with iron and manganese oxides) in "red zinc ore," and as a *silicate* ($ZnSiO_4,H_2O$) in "electric calamine" or zinc glass (Williamite).

"Franklinite" is a double oxide of zinc and iron, and "gahnite," or "zinc spinelle," a compound of zinc and aluminium oxides.

Preparation.—Zinc being volatile, its oxide cannot, like iron, be reduced in an ordinary furnace by the action of heat in the presence of reducing agents (in which case the zinc would volatilize and burn), but must be distilled.

(A.) The ore is first brought into the state of zinc oxide, either by (*α*) *calcining* the carbonate or (*β*) *roasting* the sulphide ;

Calcination—(*a*.) $ZnCO_3$ (calamine) $= ZnO + CO_2$.
Roasting. — (*β*.) $2ZnS$ (blende) $+ 3O_2 = 2ZnO + 2SO_2$.

[In process *β*, the conversion of ZnS into $ZnSO_4$ must be avoided, otherwise the $ZnSO_4$ formed would, in the after treatment, be reduced to ZnS, and so the metal in combination not be recovered.]

(B.) The oxide thus formed is now heated with half its weight of powdered coal, either in earthen retorts (Belgian process), or in a crucible closed with a luted lid, and fitted at the bottom with an exit pipe (English process), the distilled zinc in either case being collected in iron receivers (*distillation per descensum*),

$$ZnO + C = Zn + CO.$$

Before the distillation of the zinc commences, a finely divided powder, termed zinc dust, passes over. This consists of a mixture of zinc with zinc oxide and some cadmium.

Impurities and purification.—The principal impurities of zinc are *zinc oxide*, *lead*, *iron*, *tin*, *antimony*, *arsenic*, *copper*, and *cadmium*.

The separation of the *zinc oxide* is effected by skimming off the dross which collects on the surface of the melted metal. The ingots thus prepared are known as "spelter." The presence of *lead* interferes with rolling the zinc. The greater specific gravity of lead ($Pb=11{\cdot}4$; $Zn=7{\cdot}14$) enables a portion to be extracted by simply melting the alloy, the *upper* part of the melted mass, consisting of zinc, containing not more than 1·2 per cent. of lead.

The separation of *cadmium* and *arsenic* is commonly effected during distillation. These metals, being more volatile than zinc, pass over first, and burn at the mouth of the tube with a brown flame (*brown blaze*). The distillation of the pure zinc is determined by the flame assuming a bluish-white color (*blue blaze*).

If zinc be redistilled in a clay retort, a fairly pure zinc may be obtained, provided the first part of the distillate (which contains arsenic and cadmium), and the latter part (which contains lead, iron, and the less volatile constituents), are rejected.

The pure metal may be prepared by first igniting pure zinc carbonate, and distilling the oxide so formed with sugar charcoal in a porcelain retort.

Properties.—(*a*.) *Physical.* A light, hard, bluish-white crystalline (flat hexagons) metal. It melts at 773° F. (412° C.), boils at 1,904° F. (1,040° C.), and volatilizes at a red heat. At ordinary temperatures it is brittle, but between 212° and 302° F. (100° and 150° C.) it is both ductile and malleable, whilst at 410° F. (210° C.) it again becomes brittle. It distils at a bright red heat.

(β.) *Chemical.* Zinc preserves its lustre in dry air at ordinary temperatures. When heated it burns in air with a greenish-white flame, zinc oxide (ZnO), known as "*nil album*" or *philosopher's wool*, being formed. The metal rapidly tarnishes in moist air, the zinc oxide or basic carbonate formed protecting the metal underneath from further change. Cold water has no action upon it, but the metal decomposes steam at 100° C. ($Zn + H_2O = ZnO + H_2$). The haloid elements, in the presence of moisture, act freely upon it.

Dilute sulphuric and hydrochloric acids have a feeble action only upon *pure* zinc; but the action becomes energetic if a trace of platinic chloride be added to the acid solution, when hydrogen is evolved and platinum deposited on the zinc. The comparative ease with which zinc is acted on by acids depends on impurities in the metal. Thus hydrogen is commonly prepared by the action of dilute sulphuric acid on commercial zinc. If *pure* zinc be used for this purpose, the evolution of hydrogen soon ceases, from the metal becoming covered with hydrogen globules. If a piece of copper be now introduced into the mixture, the copper (which is electro-negative towards the zinc) attracts the electro-positive hydrogen, thus effecting a continuous liberation of the gas.

Zinc dissolves in cold nitric acid, no free hydrogen, but ammonia being evolved. In hot nitric acid, ammonia, nitrogen and the lower oxides of nitrogen are formed. With cold strong sulphuric acid, or with hot dilute sulphuric acid, both hydrogen and sulphuretted hydrogen are evolved.

Solutions of the caustic alkalies act readily upon zinc, hydrogen and zinc oxide (which latter is soluble in the alkaline solution, thereby forming a double salt), being formed ($Zn + 2KHO = ZnO,K_2O + H_2$).

Zinc is a powerful base. Placed in many metallic solutions it precipitates the metal, and in its place is itself dissolved.

Uses.—Zinc is employed for voltaic batteries—also in building operations as a substitute for lead, its advantage being its comparative lightness. Although not malleable at common temperatures, it is perfectly malleable at 212° F. (100° C.). Brass is an alloy of copper (2 parts) and zinc (1 part). German silver is brass with a small quantity of nickel added. *Galvanized iron* consists of iron coated with zinc, and is prepared by dipping *clean* iron into melted zinc covered with sal-ammoniac. By this means the surface of the melted zinc is kept free from oxidation, zinc oxide being soluble in NH_4Cl. If this were not done the zinc oxide adhering to the iron plate in the act of dipping would prevent its becoming uniformly coated. In galvanized iron we obtain the strength of the iron, which is much greater than that of zinc, together with the preservative action of the zinc, any ZnO formed itself acting as a protective varnish.

Zinc dust is used in the laboratory as a reducing agent. The metal is also employed in the desilverization of lead.

Compounds of Zinc ($Zn = 65$).

	COMPOUNDS.	Formula (Common).	Molecular Weight of Anhydrous Compound.	Specific Gravity of Crystal.	= to Zn or ZnO per cent. of Anhydrous Salt.
1	Zinc oxide..	ZnO	81	5·612	$Zn = 80·24$
2	,, hydrated oxide..	ZnH_2O_2	99		$Zn = 65·65$
3	,, chloride	$ZnCl_2$	136	2·753	$Zn = 47·79$
4	,, bromide	$ZnBr_2$			
5	,, iodide	ZnI_2			
6	,, fluoride	ZnF_2			
7	,, silico-fluoride ..	$SiZnF_6,6H_2O$			
8	,, sulphide (blende)	ZnS	97	4·1	$Zn = 67·01$
9	,, pentasulphide ..	ZnS_5			
10	,, nitride	Zn_3N_2			
11	,, phosphide.. ..	Zn_3P_2			
12	,, arsenide	Zn_3As_2			
13	,, antimonide ..	Zn_3Sb_2			
14	,, sulphate (white vitriol)	$ZnSO_4,7H_2O$	161+126	1·931	$Zn = 40·37$
15	,, carbonate	$ZnCO_3$	125	4·4	$ZnO = 64·8$
16	,, nitrate	$Zn2(NO_3)$ $6H_2O$	189+108		

(1.) **Zinc Oxide** ($ZnO=81$, Specific gravity, 5·6) occurs native as *spartalite.*

Preparation.—(*a.*) By the combustion of zinc in air (*philosopher's wool*). (*β.*) By the ignition of the basic carbonate (prepared by adding an alkaline carbonate to a solution of a zinc salt).

Properties, etc.—The oxide is employed as a pigment (zinc-white) in the place of white lead, its advantage being that it is not blackened by sulphuretted hydrogen, and that its use does not affect the health of workpeople, and its disadvantage, that it more easily peels off on account of its not combining chemically, like oxide of lead, with the oil. When heated, the white oxide turns yellow, but again becomes white on cooling. Heated in the oxy-hydrogen flame, it emits a brilliant light, appearing phosphorescent as it cools. It is insoluble in water, but readily soluble in acids. "Tutty," a substance obtained from the flues of brass furnaces, is an impure zinc oxide.

(2.) **The Hydrated Oxide** (ZnH_2O_2) is obtained by the action of sodic, ammonic or potassic hydrate on solutions of zinc salts ($ZnSO_4+2KHO=ZnH_2O_2+K_2SO_4$), the precipitate formed being soluble if an excess of the precipitant be added. It is decomposed by heat into water and zinc oxide. Dissolved in excess of caustic soda, a soluble salt (sodium zincate) is formed, in which the zinc oxide may be regarded as acting the part of an acid.

(3.) **Zinc Chloride** ($ZnCl_2$) is prepared by dissolving zinc in hydrochloric acid, or by heating the metal in chlorine. On evaporating the hydrochloric acid solution to dryness, and distilling the residue, the chloride may be obtained as a white, deliquescent, fusible, corrosive solid. It is freely soluble in water and in alcohol. In a concentrated solution it is a powerful caustic. It absorbs ammonia gas freely. It fuses at about 212° F. (100° C.), sublimes at a higher temperature, and distils at a heat of 1292° F. (700° C.) By heating together chloride and oxide of zinc, and precipitating with water, a number of *oxy-chlorides* may be prepared. By boiling the oxide and chloride together, a plastic mass is obtained, which speedily becomes hard, and is used as a stopping for teeth. (*See* MAGNESIUM, p. 389.)

The solution of the chloride (known as *Burnett's Disinfecting Fluid*) is a powerful antiseptic and deodorizer, its activity being dependent on the power it possesses of absorbing the offensive products of putrefaction. It is used as a caustic agent in medicine. With the alkaline chlorides, zinc chloride forms double salts, the *zinc ammonic chloride* ($2NH_4Cl, ZnCl_2$) being used as a soldering flux to remove the film of oxide from the surface of metals. The chloride abstracts water from many organic bodies.

(**4** to **7.**) *Zinc bromide* ($ZnBr_2$), *zinc iodide* (ZnI_2) (prepared by heating together zinc filings and iodine), *zinc fluoride* (ZnF_2) (prepared by dissolving zinc in aqueous hydrofluoric acid), and a *zinc silico-fluoride* or *fluosilicate* ($ZnSiF_6,6H_2O$) are known.

(**8** and **9.**) **Zinc Sulphide** ($ZnS=97$) occurs native as blende, either in masses, or in dark-colored crystals (rhombic dodecahedra) (*black Jack*), or as Wurtzite (hexagonal prisms). A *white hydrated sulphide* (which, dried at ordinary temperatures, has the composition ZnS,H_2O, but if dried at 212° F., of $2ZnS,H_2O$) may be prepared by the action of hydric-ammonic sulphide on a solution of a zinc salt. Zinc sulphide is not precipitated by sulphuretted hydrogen in mineral acid solutions. The precipitated sulphide is insoluble in water or in acetic acid, but is soluble in the mineral acids. It may be sublimed by heat in a current of H_2S.

A *zinc pentasulphide* (ZnS_5) may be prepared by adding potassium pentasulphide to a neutral solution of a zinc salt.

(**10** to **13.**) **Zinc Nitride** (Zn_3N_2) may be prepared by the action of heat on zinc diamine in the absence of air [$3Zn(NH_2)_2 = Zn_3N_2 + 4NH_3$]; **Zinc Phosphide** ($Zn_3P_2$), by heating zinc in phosphorus vapor; **Zinc Arsenide** (Zn_3As_2), by heating together zinc and arsenic, and **Zinc Antimonides** (Zn_3Sb_2 and Zn_2Sb_2), by fusing together zinc and antimony in proper atomic proportions.

(**14.**) **Zinc Sulphate** (*white vitriol*, $ZnSO_4,7H_2O$).

Preparation.—By roasting zinc sulphide *at a low temperature.* [If roasted *at a high temperature* an oxide would be formed.] The mass after roasting is dissolved in water and the solution crystallised. The sulphate also occurs as a residue in the common process of preparing hydrogen [viz., by acting on zinc with dilute sulphuric acid].

Properties.—A white, crystalline (four-sided prisms), efflorescent salt (isomorphous with Epsom salt), insoluble in alcohol, soluble in water (1 in 2·5 aq. at 60° F., and 1 in 1 at 212° F.). When heated, it melts in its own water of crystallisation. At a temperature above 104° F. (40° C.) the solution deposits crystals having the composition $ZnSO_4,6H_2O$. If the ordinary sulphate (*i.e.*, $ZnSO_4,7H_2O$) be heated to 212° F. it gives up $6H_2O$, becoming $ZnSO_4,H_2O$, and at 400° F. becomes anhydrous ($ZnSO_4$). If the anhydrous salt be heated to a high temperature, it evolves O and SO_2, a basic salt being formed, which if dissolved in water deposits crystals of $ZnSO_4,3ZnO,2H_2O$. At a white heat the anhydrous sulphate becomes ZnO. With potassic and ammonic sulphates, zinc sulphate forms double salts (such as $ZnK_2(SO_4)_2,6H_2O$) isomorphous with the corresponding magnesium salts.

White vitriol is used in calico printing, in medicine as an emetic, etc.

(15.) **Zinc Carbonate** ($ZnCO_3=125$) is found native as *calamine*, so called from its tendency to form reed-like masses, and as "Zinc spar." The body termed "electric calamine" is a silicate.

When a soluble carbonate is added to a solution of a zinc salt, a *hydrated zinc oxycarbonate* (a basic carbonate) is formed ($8ZnO,3CO_2,6H_2O$), which is soluble in ammonium carbonate, but not in the carbonates of soda or potash. It readily loses CO_2 when ignited.

(16.) **Zinc Nitrate** ($Zn2NO_36H_2O$) separates as four-sided prisms from a solution of the oxide in nitric acid. It is soluble in water and alcohol. It is a deliquescent salt, and fuses at 97° F. (36° C.) in its water of crystallisation. At 212° F. (100° C.) it gives up water and nitric acid, yielding a basic salt.

A Zinc Phosphate ($Zn_3P_2O_8$) may be prepared by adding hydric sodic phosphate to a solution of a zinc salt.

REACTIONS OF ZINC COMPOUNDS.

[Salts white, unless the acid be colored.]

1. Non-luminous flame : No effect.

2. Spectrum : Spark spectrum shows lines in red and blue.

3. *Caustic alkalies and ammonia ;* A white ppt. of ZnH_2O_2, soluble in excess.

4. *Alkaline carbonates ;* A white precipitate of a basic carbonate, soluble in excess of ammonium carbonate, but not in excess of sodium or potassium carbonates.

5. *Sulphuretted hydrogen ;* A white ppt. of hydrated sulphide in alkaline solutions ($ZnS,(H_2O)_n$). [In neutral solutions, precipitation takes place, but is never complete.]

6. *Potassium ferrocyanide;* A white ppt. of zinc ferrocyanide.

7. *Heated on charcoal with blowpipe.* In outer flame an incrustation, which is yellow when hot and white when cold. (Moisten the cold incrustation with a solution of cobalt nitrate, and again heat, when a fine green-colored mass is obtained (Rinmann's green).)

COBALT.

Atomic Weight 58·6. *Atomicity dyad, as in cobaltous compounds* ($Co''O$), *and hexad* (*pseudo-triad*) *in cobaltic compounds* (Co_2O_3). *Specific gravity,* 8·5.

History.—Since the sixteenth century, roasted cobalt ores have been used for producing a blue glass. The metal was discovered by Brandt (1733). (Κόβαλος *a goblin.*)

Natural History.—It is never met with in a free state in nature, except in meteoric iron. It occurs as an *arsenide*, in "tin white cobalt" or *speiss cobalt* ($CoAs_2$), and as an *arsenio-sulphide* in cobalt glance ($CoAsS$). Its ores commonly contain nickel, copper, iron, manganese, etc.

Preparation.—(1.) By heating cobalt oxalate (CoC_2O_4) as follows :—

The ore is first roasted (to get rid of some of the sulphur and arsenic). The residue (*zaffre*) is then dissolved in HCl with a little nitric acid. H_2S is passed through this solution (As, Cu and Pb being precipitated). The iron is again oxidised with nitric acid, and sodium carbonate added until the solution is neutral, $Fe_2H_6O_6$ being precipitated. To the filtered solution an excess of sodium carbonate is now added, to throw down the mixed carbonates of cobalt and nickel. These are converted into oxalates by digesting in a strong solution of oxalic acid. The oxalates thus obtained are dissolved in strong ammonia and the solution exposed to the air, when oxalate of nickel is precipitated, and oxalate of cobalt remains in solution. The clear solution is evaporated to dryness, dissolved in HCl, and reprecipitated with oxalic acid. The cobalt oxalate thus obtained is reduced by heating in a crucible with dry common salt.

(2.) Cobalt may be prepared from its oxide by dissolving in HCl, and adding ammonia in excess in the presence of ammonic chloride, to precipitate any ferric hydrate present. By exposing the clear solution to air, and afterwards treating with HCl and boiling, a red crystalline compound of $Co_2Cl_6(NH_3)_{10}$ is obtained, which may be reduced (as well as any cobalt oxide present) by heating in a current of hydrogen.

Properties.—(*a.*) *Physical.* A white, hard metal, taking a high polish, ductile and magnetic, attracted by the magnet even when red hot. It is very infusible, although less so than iron, and possesses great tenacity. Specific gravity, 8·5 to 8·7.

(β.) *Chemical.* It oxidises when heated in air. It is permanent in dry air, but tarnishes when the air is moist. The mineral acids (even when dilute) act on it freely, hydrogen being evolved with dilute sulphuric or hydrochloric acids, SO_2 with strong sulphuric acid, and nitric oxide with nitric acid, cobaltous salts in each case resulting.

Compounds of Cobalt (Co=59).

	COMPOUNDS.	General Formula.	Molecular Weight.	Co per cent.
1	Cobaltous oxide	CoO	75	78·66
2	,, hydrate	CoH_2O_2	93	63·44
3	Cobaltic oxide (sesquioxide)	Co_2O_3	166	71·08
4	,, hydrate	$Co_2H_6O_6$		
5	Cobalto-cobaltic oxide	CoO,Co_2O_3	241	73·44
6	Cobaltous chloride	$Co''Cl_2 6H_2O$	130+108	45·38
7	Cobaltic chloride	Co_2Cl_6	331	35·64
8	Cobaltous sulphide	CoS	91	64·83
9	Cobaltic sesquisulphide	Co_2S_3		
10	,, disulphide	CoS_2	123	
11	Cobaltous sulphate	$Co''SO_4,7H_2O$	155+126	38·06
12	,, nitrate	$Co2NO_3,6H_2O$	183+108	32·24
13	,, carbonate	$CoCO_3$	119	
14	,, arsenate	$Co_3As_2O_8 8H_2O$		
15	Silicates of cobalt			
16	Cobaltous phosphate	$Co_3P_2O_8$		
17	,, oxalate	CoC_2O_4		

OXIDES OF COBALT, ETC.

1. Cobaltous oxide	CoO.
2. ,, hydrate	$CoO,H_2O = CoH_2O_2$.
3. Cobaltic oxide	Co_2O_3.
4. ,, hydrate	$Co_2O_3.3H_2O = Co_2H_6O_6$.
5. Cobalto-cobaltic oxide	Co_3O_4 (or Co_2O_3,CoO).

(1 and 2.) Cobaltous Oxide.—*Protoxide of Cobalt* (Co″O).

Preparation.—The hydrate (CoH_2O_2) is prepared by adding caustic soda to a solution of cobaltous chloride and boiling. The precipitate first formed is a basic chloride (of a lavender colour), which on boiling becomes the blue cobaltous hydrate. If this precipitate be ignited with exclusion of air, it leaves cobaltous oxide (CoO).

Properties.—Cobaltous oxide is a brown-colored body, becoming cobalto-cobaltic oxide (Co_3O_4) when heated in air. It is soluble in ammonia and in acids, the solution being blue when concentrated, and pink when dilute. It is used for painting on porcelain.

It forms cobaltous salts (in which the metal acts as a dyad) by combination with acids (*e.g.* $Co''CO_3$).

(3 and 4.) **Cobaltic Oxide,** or *sesquioxide of cobalt* (Co_2O_3).

Preparation.—(1.) (*As a hydrate,* $Co_2O_3,3H_2O$.) (*a.*) By passing chlorine through water in which the hydrated cobaltous oxide is suspended ($3CoH_2O_2 + Cl_2 = Co_2H_6O_6 + CoCl_2$) ; or (*β.*) by adding an alkaline hypochlorite (*bleaching powder*) to the solution of a cobaltous salt.

(2.) (*Anhydrous.*) By gently igniting cobaltic hydrate or cobaltous nitrate.

Properties.—A black substance, insoluble in water, but soluble in cold acids. Heated to a high temperature, it becomes (CoO,Co_2O_3). It is a feeble base, the cobaltic salts containing a double atom of the metal of hexad atomicity. The acid solutions of cobaltic salts rapidly change to cobaltous salts.

(5.) **Cobalto-cobaltic Oxide** (Co_3O_4 *or* Co_2O_3,CoO).—This oxide is formed by the action of heat on the other cobalt oxides.

(6.) **Cobaltous Chloride** ($CoCl_2$).

Preparation.—(1.) By passing chlorine over the metal.

(2.) By dissolving the oxide in hydrochloric acid, evaporating and drying at 284° F. (140° C.).

Properties.—The hydrate $CoCl_2,6H_2O$ is *red,* and the anhydrous cobaltous chloride *blue.* "*Sympathetic ink*" is a dilute solution of this salt, the changes of color to which it is subject being dependent on different degrees of hydration. The addition of traces of zinc, iron, or copper chlorides varies the tints thus produced.

Cobaltous Bromide and **Iodide** are formed by digesting finely divided cobalt with iodine or bromine in water, and **Cobaltous fluoride** by acting on cobaltous carbonate with hydrofluoric acid.

(7.) **Cobaltic Chloride** (Co_2Cl_6) is prepared by saturating $CoCl_2$ with chlorine.

(8.) **Cobaltous Sulphide** (CoS) is found native (Sp. gr. 5·45). It is formed when sulphur and cobalt are fused together. A hydrated sulphide (soluble in HCl with evolution of H_2S) is formed when ammonic sulphide is added to a solution of cobaltous salts.

(9, 10.) Other sulphides, viz. CoS_2, Co_2S_3 and Co_3S_4, have been obtained.

(11.) **Cobaltous Sulphate** ($CoSO_4,7H_2O$). It occurs native as *cobalt vitriol.* Sp. gr. 1·9.

Preparation.—By dissolving the carbonate or oxide in sulphuric acid.

Properties.—Dark red crystals, isomorphous with ferrous sulphate. It forms double sulphates with the alkaline sulphates, resembling in this respect zinc and certain other metals.

(12.) **Cobaltous Nitrate** ($Co2NO_3,6H_2O$).

Preparation.—By dissolving the metal, its oxide or carbonate, in nitric acid.

Properties.—Red deliquescent crystals, soluble in water. It is used as a blow-pipe reagent :—Thus a *zinc* compound, when moistened with it and heated, turns green, a *magnesium* compound changing pink, and an *aluminium* compound blue.

(13.) **Cobaltous Carbonate** ($CoCO_3$). A *basic carbonate* ($2CoCO_3$, $3CoH_2O_2,H_2O$) is produced when sodic carbonate is added to a solution of a cobaltous salt. The normal carbonate $CoCO_3$ may be prepared by heating cobaltous chloride with a hydric sodic carbonate solution saturated with CO_2, and afterwards exposing the mixture to a low temperature.

(15.) **Cobalt Silicates.**—*Smalt* is a mixed silicate of potash and cobalt. *Preparation.*—The ore is roasted at a low temperature to oxidize the cobalt, and the mass fused with sand and potash. (The Ni, Fe, Cu, Bi, etc., present, collects at the bottom of the pot.) The glass formed is then ground under water. It contains from 6 to 10 per cent. of cobalt.

The *cobaltic salts* are only known in solution. Certain double cobaltic salts of some stability have been prepared. *Potassic cobaltic nitrite* ($Co3NO_2,2KNO_2,H_2O$) is a yellow crystalline body, formed when an aqueous solution of potassic nitrite is added to one of a cobaltous salt acidulated with acetic acid.

"*Thénard's blue*" is a compound of cobalt and alumina. "*Zaffre*" is a roasted mixture of cobalt ore and sand. "*Rinmann's green*" is a compound of the oxides of cobalt and zinc. "*Smalt*" is powdered glass, colored by oxide of cobalt.

(16.) **Cobaltous Phosphate** ($Co_3P_2O_8$) occurs as a rose-red precipitate on mixing solutions of sodium phosphate and a cobaltous salt.

(17.) **Cobaltous Oxalate** (CoC_2O_4) is formed as a pink powder when oxalic acid is added to a cobaltous salt.

Cobaltamines.

AMMONIA COMPOUNDS OF COBALT.

The unstable cobaltic chloride forms, with ammonia, a series of stable and remarkable compounds, called "cobaltamines," which may be expressed (whatever their real constitution, which is doubtful) as additive compounds of gaseous ammonia with cobalt chloride. Thus we have, besides others—

(1.) $CoCl_3,6NH_3$ (luteo-cobaltic chloride).

(2.) $CoCl_3,5NH_3$ (purpureo-cobaltic chloride).

These bodies are formed by mixing an aqueous solution of cobaltous chloride with excess of strong ammonia, exposing the solution to the air, and boiling with hydrochloric acid.

If the watery solution of these chlorides be digested with silver oxide, *an alkaline liquid* (the hydrate) results, AgCl being precipitated. The separation of the base so formed has not been effected, as decomposition, with evolution of ammonia, takes place so soon as concentration is attempted.

Further. The anhydrous cobaltous chloride absorbs gaseous ammonia, yielding the compound $CoCl_2,6NH_3$, which by heat can be converted into $CoCl_2,2NH_3$. These compounds form double chlorides with the chlorides of gold and platinum. On exposure to the air, their solutions absorb oxygen, brown compounds (*peroxidized ammonio-cobalt salts*) of a very complex nature, consisting of ammonia and various oxides of cobalt, resulting.

REACTIONS OF COBALT COMPOUNDS.

Heated with sodic carbonate on charcoal, white metallic particles, which will be found to be magnetic, are formed.

Flame and spectrum.—No action.

Borax bead.—Deep blue in both flames.

Caustic alkalies.—Blue ppt., becoming red on boiling (CoH_2O_2).

Ammonia (as with caustic alkalies). The precipitate is soluble in excess, the solution being red, but becoming brown on exposure. [No ppt. in presence of ammonia salts.]

Sulphuretted Hydrogen.—No ppt. in acid solution.

Ammonium Sulphide.—Black ppt. (CoS,H_2O), insoluble in alkalies or in alkaline sulphides. Soluble in aqua regia.

Potassium Ferrocyanide.—Green ppt. (Co_2FeCy_6).

Potassium Ferricyanide.—Reddish ppt. ($Co_3Fe_2Cy_{12}$).

Potassium Cyanide.—A pale brown ppt. ($CoCy_2$), soluble in excess of the KCy ($=2KCy,CoCy_2$). [From this solution HCl precipitates $CoCy_2$.] If the solution of the double salt containing an excess of potassic cyanide be boiled, hydrogen is evolved, and potassium cobalticyanide ($3KCy,CoCy_3$) formed [$2KCy,CoCy_2+2KCy+H_2O=3KCy,CoCy_3+KHO+H$]. This solution gives no ppt. either with acids, or with ammonic sulphate, or with sodic hypochlorite.

[NOTE.—With nickel the double salt ($3KCyNiCy_3$) is formed, but the solution is precipitated by acids ($NiCy_2$), and if boiled with sodic hypochlorite gives a black ppt. of ($Ni_2H_6O_6$).]

NICKEL (Ni).

Atomic weight, 58·6. *Atomicity dyad, as in nickelous compounds* ($NiCl_2$) *to hexad, and in nickelic compounds a pseudo-triad, the double atom being hexvalent* (Ni_2O_3).

History.—Discovered by Cronstedt (1751).

Natural History.—It is found as an *arsenide*, as kupper-nickel ($NiAs$) and as arsenical nickel ($NiAs_2$) ; and also as an *arsenio-sulphide* in grey nickel ore or nickel glance ($NiAs_2,NiS_2$). It occurs in meteorites. It is invariably associated in nature with cobalt. A mineral called garnierite (nickelous silicate) found in New Caledonia is however said to be free from cobalt.

Preparation.—*See* Cobalt (p. 424). (1.) By roasting cobalt ore, an oxide of cobalt is formed. When this is fused with quartz and potassic silicate, it forms a blue glass (*smalt*), consisting of a mixture of the silicates of cobalt and potash. The fused metallic residue which collects at the bottom of the crucible, constitutes "*speiss*," a mixture of the sulphides and arsenides of nickel, iron, and copper. From this residue metallic nickel is obtained.

(2.) By igniting the precipitated oxalate (p. 424).

Properties.—(*a.*) *Physical.* A hard, silvery-white metal, ductile and malleable, more fusible, but of greater tenacity than iron. It is somewhat magnetic, the magnetism being lost when the metal is heated to 626° F. (330° C.). Specific gravity, 8·9.

(β.) *Chemical.* It is permanent in air at ordinary temperatures, dry or moist. It oxidizes when heated in air. It decomposes steam at a red heat, becoming NiO. Dilute nitric acid dissolves it readily. Strong nitric acid changes it into a passive condition, as in the case of iron (p. 404). Hydrochloric and dilute sulphuric acids dissolve it slowly, hydrogen being evolved. It is acted on by both chlorine and bromine.

Uses.—For rendering brass (an alloy of copper and zinc) white (*German silver, packfong, tutenag*). For nickel-plating, the deposit of the metal being effected by precipitating it with the galvanic current from the double cyanide.

Compounds of Nickel (Ni=59).

	COMPOUNDS.	Ordinary Formula.	Molecular Weight.	Specific Gravity.	Ni
1	Nickelous oxide	NiO	75	5·75	78·67
2	Hydrated nickelous oxide	NiH_2O_2	93		63·44
3	Nickelic oxide, etc. ..	Ni_2O_3	166		71·08
4	„ hydrate	$Ni_2H_6O_6$			
5	Nickelous chloride, etc.	$NiCl_2$ [$NiBr_2$; NiI_2; NiF_2]	130		45·38
6	„ sulphide ..	NiS	91		64·83
7	Nickelic sulphide	NiS_2	123		
8	Nickelous sulphate ..	$NiSO_4,7H_2O$	155+126	2·037	38·06
9	„ nitrate	$Ni2NO_3,6H_2O$	183+108		
10	„ carbonate ..	$NiCO_3$	119		32·24
11	„ phosphate ..	$Ni_3P_2O_8$			49·57
12	„ arsenate.. ..	$Ni_3As_2O_8,8H_2O$			

Compounds of Nickel with Oxygen, etc.

Nickelous oxide	NiO.
„ hydrate	NiH_2O_2.
Nickelic oxide	Ni_2O_3.
„ hydrate	$Ni_2H_6O_6$.

(1, 2.) **Nickelous Oxide.**—(*Protoxide of Nickel*) (NiO). Found native.

Preparation.—(1.) (*Anhydrous.*) By the ignition of the nitrate or carbonate.

(2.) (*As a hydrate*, NiH_2O_2.) By adding potassic hydrate to a boiling solution of a nickelous salt.

Properties.—The hydrate, as well as its solution in acids, is green. It is soluble in ammonia and in ammonic chloride, but is insoluble in sodic and potassic hydrates.

(3.) **Nickelic Oxide** (Ni_2O_3). A black powder, prepared by carefully heating the nitrate. Forms no salts with acids. Soluble in hydrochloric and sulphuric acids with evolution of chlorine and of oxygen respectively. Soluble in ammonia, with evolution of nitrogen.

The hydrate ($Ni_2H_6O_6$) is prepared by passing chlorine through water, in which the nickelous hydrate is suspended, or by precipitating a salt of nickel with sodium hypochlorite. It is a black powder, decomposed by heat.

(5.) **Nickelous Chloride** ($NiCl_2$). *Preparation.*—By dissolving the oxide or carbonate in hydrochloric acid, and evaporating to dryness. Small green crystals ($NiCl_2,6H_2O$), becoming yellow when dried.

Note.—Nickel yields no ammonium compounds corresponding to the cobaltamines (p. 427).

Nickelous *Bromide and Iodide* are prepared by heating the metal in the vapor of bromine and iodine respectively. The *fluoride* (NiF_2) is prepared by evaporating down a solution of the carbonate in hydrofluoric acid.

(6.) **Nickelous Sulphide** (NiS) occurs native as "millerite" or "capillary pyrites." It is prepared when nickel and sulphur are heated together, and is precipitated as a hydrate by the action of an alkaline sulphide on a salt of nickel. It oxidises slowly by exposure to air.

(7.) **Nickelic Sulphide** (NiS_2).

Preparation.—By fusing a mixture of the carbonate with sodium carbonate and excess of sulphur. A dark iron-grey powder.

(8.) **Nickelous Sulphate** ($NiSO_4,7H_2O$).

Preparation.—By dissolving the metal, its oxide or carbonate, in sulphuric acid.

Properties.—A green crystalline salt (rhombic prisms), soluble in water (1 in 3 aq. at 60° F.), and insoluble in alcohol. At 104° F. (40° C.)

it becomes $NiSO_4,6H_2O$. It forms double salts with alkaline sulphates, isomorphous with the corresponding magnesium salts. The ammonic nickelous sulphate is used in electroplating. The anhydrous salt absorbs ammonia, forming $NiSO_4,6NH_3$.

(9.) **Nickelous Nitrate** ($Ni2NO_3,6H_2O$).

Preparation.—By dissolving the metal, its oxide or carbonate, in nitric acid. The crystals are soluble and deliquescent.

Nickelous Nitrite ($Ni2NO_2$) forms reddish-yellow crystals. The salt may be prepared by decomposing the sulphate with barium nitrite.

REACTION OF NICKEL COMPOUNDS.

Heated with sodium carbonate on charcoal in the reducing flame, nickel compounds yield white magnetic particles of the metal.

Borax bead.—In oxidizing flame, the bead becomes violet whilst hot, and reddish-brown when cold; in the reducing flame, the bead becomes grey from the separation of nickel.

Non-luminous flame—No action.

[Anhydrous compounds are yellow. The crystals (aquates) apple-green.]

Caustic Alkalies; pale green ppt. (NiH_2O_2), not altered by exposure nor by boiling.

Ammonia; pale-green ppt. (NiH_2O_2), soluble in excess, the solution becoming of a deep blue color. [No ppt. in the presence of ammonium salts.]

Sulphuretted Hydrogen—No ppt. in acid solutions.

Ammonic Sulphide.—A black ppt. (NiS,H_2O), slightly soluble in excess (ppt. not very soluble in dilute HCl).

Potassium Ferrocyanide.—A greenish ppt. (Ni_2FeCy_6).

Potassium Ferricyanide.—A yellowish-brown ppt. ($Ni_3Fe_2Cy_{12}$).

Potassium Cyanide.—A yellowish ppt. ($NiCy_2$), soluble in excess from the formation of a double salt. From this solution the $NiCy_2$ is re-precipitated by acids as $NiCy_2$, or if heated with sodic hypochlorite, the nickel is precipitated as a black nickelic hydrate. (*Confer* Cobalt, p. 428.)

URANIUM (U).

Atomic weight, 238·5. *Atomicity, tetrad in uranous compounds (as* UO_2 ; UCl_4)*, and hexad in uranic compounds (as* UO_3).

History.—Discovered by Klaproth (1789) in pitchblende. Isolated by Péligot (1842).

Natural History.—Not found native. It occurs as an *oxide* (pitchblende, $UO,2U_2O_3 = U_3O_8$ with Cu, Pb, Fe, As, etc.), and also as a *phosphate* (uranite and chalcolite) and *carbonate* (liebigite).

Preparation.—By decomposing the chloride with metallic sodium or potassium, using potassic chloride as a flux.

Properties.—A grey, silvery, somewhat malleable metal. Sp. gr. 18·4. It is but very slightly oxidized by air or by water at common temperatures, but burns in air, when heated yielding U_3O_8. It is soluble in sulphuric and hydrochloric acids. It does not decompose water even at its boiling point. It combines energetically with sulphur and chlorine.

Certain theoretical considerations (viz., its specific heat, the vapor density of several of its compounds, and its position in Mendeleef's table) have led chemists to double the former atomic weight (at one time given as 60, and another time 120) of uranium (page 55). As yet the specific heat has not been determined. Mendeleef, it will be noted, makes it an analogue of chromium, molybdenum and tungsten.

Uses.—In enamel painting, and for coloring glass for optical and electrical purposes.

Compounds of Uranium ($U = 240$).

	COMPOUNDS.		Ordinary Formula.	Molecular Weight.
1	Oxides..	Uranous oxide	UO_2	272
2		Uranic ,, ...	UO_3	288
3		Peruranic anhydride ..	UO_4	304
4		,, (green oxide)	U_3O_8	
5		,, (black oxide)	U_2O_5	
6	Chlorides	Uranous chloride	UCl_4	382
7		Uranic ,, ...	UCl_5	437·5
8		,, sesquichloride..	U_2Cl_6	713
9		Uranous bromide	UBr_4	
10		,, fluoride	UF_4	
11		Uranium oxychloride ..	UCl_2O_2	
12		,, oxybromide ..	UBr_2O_2	
13		,, oxyfluoride ..	UF_2O_2	
14	Sulphides	Uranous sulphide.. ..	US_2	304
15		Uranylic ,, ...	$(UO_2)S$	
16	Oxy-salts	Uranous sulphate.. ..	$U2SO_4$	
17		Uranic (nylic) sulphates	$(UO_2)''SO_43H_2O$	
18		,, pyrosulphate ..	$(UO_2)''S_2O_7$	

COMPOUNDS OF URANIUM.

(1.) Uranous Oxide (UO_2). A brown powder, produced when the higher oxides are heated in a current of hydrogen. It is insoluble in dilute HCl, but soluble in strong acids, from which solutions uranous hydrate (UH_4O_4) is precipitated on the addition of alkalies.

When UO_2 is heated in a current of chlorine, an oxychloride (uranylic chloride, UO_2Cl_2) is formed. This compound forms well-marked double salts with alkaline chlorides (*e.g.*, $UO_2Cl_2,2KCl,2H_2O$).

(2.) Uranic Oxide (*uranic anhydride*) (UO_3). A brown powder, produced when the nitrate is heated to 482° F. (250° C.). It can play the part of both acid and base. As an *acid* it unites with alkalies to form a class termed the *uranates*. As a *base* it combines with acids to form salts, the radical uranyl (UO_2), acting as a dyad metal.

The oxides of uranium have therefore to be regarded from two points of view: (A) as acids, and (B) as bases.

(A.) The *Uranates.*—These are salts where uranic oxide (UO_3) unites with strong bases and plays the part of an acid (*e.g.* $K_2U_2O_7$, or $K_2O,2UO_3$, potassic uranate, a salt corresponding to potassic bichromate, $K_2O,2CrO_3$). All the uranates are insoluble in water. The ammonium salt dissolves in a cold solution of ammonic carbonate, and on ignition leaves the green oxide U_3O_8. The sodium salt known as uranium yellow ($Na_2O,2UO_3$), prepared by fusing uranic oxide with sodic carbonate, is used in the preparation of uranium glass.

Certain *peruranates* (*e.g.* sodic peruranates $2Na_2O,UO_4$), are said to have been prepared by the action of peroxide of hydrogen upon alkaline solutions of uranic salts.

(B.) *Uranyl.*—It was noted by Péligot that the oxide UO_2 was disposed to act as a dyad metallic element, the normal uranic salts being formed by a combination of UO_2 with two molecules of a monobasic acid. To this dyad radical he gave the name *Uranyl*, *e.g.*—

$(UO_2)''\ 2NO_3,6H_2O =$ Uranic (uranyl) nitrate.
$(UO_2)''\ SO_4,3H_2O =$,, ,, sulphate.
$(UO_2)''\ HPO_4,4H_2O =$,, ,, phosphate.
$(UO_2)K_2 2SO_4 2H_2O =$,, ,, potassic sulphate.

To express this view of their constitution, the uranic salts have been called uranyl salts.

The uranyl acetate $[(UO_2)(C_2H_3O_2)_2]$ is used for the quantitative estimation of phosphoric acid, forming in the presence of ammonium chloride, the insoluble uranyl ammonium-phosphate $[(UO_2)NH_4PO_4]$.

(4, 5.) Oxides of the composition $U_3O_8 = UO_2 + 2UO_3$ (green oxide, or sesquioxide of uranium), prepared by gently heating UO_2 or UO_3 in air; and $U_2O_5 (= UO_2 + UO_3)$ (black oxide of uranium), prepared by strongly heating the other oxides of uranium in air, are known.

(6, 8.) **Uranous Chloride** (UCl_4) is a dark green, deliquescent, volatile and crystalline body, prepared by heating any of the uranium oxides mixed with carbon in a current of dry chlorine. Its solutions absorb oxygen from the air. By heating UCl_4 in a current of hydrogen, dark brown needle crystals of the sesquichloride (U_2Cl_6) are formed.

(7.) **Uranic Chloride** (UCl_5). A volatile deliquescent solid, prepared along with UCl_4 by the process described above, provided the temperature be not so high as to effect decomposition. At 248° F.

(120° C.) it is decomposed into UCl_4 and free chlorine. When heated in dry ammonia, a uranium nitride is said to be formed.

(14.) **Uranous Sulphide** (US_2) may be prepared, both in a crystalline and an amorphous form, by the action of H_2S on uranous chloride. When exposed to the air H_2S is evolved.

(15.) **Uranic (-nylic) Sulphide,** $(UO_2)S$, a black powder, formed by the action of ammonic sulphide on uranic nitrate. Soluble in ammonic carbonate.

REACTIONS OF URANIUM COMPOUNDS.

Non-luminous flame. No action.

To the borax bead, uranium imparts a yellow color in the oxidizing flame, and a green color in the reducing flame. Fluorescent in bright light.

Solution.—(A.) URANOUS COMPOUNDS (generally of a green color).

(1.) *Alkalies.*—A gelatinous brown ppt. (UH_4O_4), becoming after a time yellow (UO_3).

(2.) *Ammonic sulphide.*—A black ppt. (US_2).

(B.) URANIC COMPOUNDS (yellow color).

(1.) *Ammonia and caustic alkalies.*—A yellow ppt. of an alkaline uranate.

(2.) *Ammonic sulphide.*—A yellowish brown ppt. (H_2S gives no ppt. in acid solutions).

(3.) *Ammonic carbonate.*—A yellow ppt. $[(UO_2)CO_3 + 2NH_4CO_3]$, slightly soluble in water and in an excess of precipitant.

(4.) *Potassic ferrocyanide.*—A reddish brown precipitate.

[To detect uranium in a mineral, dissolve the mineral in nitric acid, dilute the solution with water, boil with an excess of sodic carbonate, filter, and precipitate the U_2O_3 with potassic hydrate.]

INDIUM (In).

Atomic weight, 113·4. *Specific gravity,* 7·4. *Fuses at* 349° F. (176° C.). *Atomicity* ($'''$), *triad as in* $InCl_3$. *Specific heat,* 0·057.

History.—Discovered (1863) by Reich and Richter in the Freiberg zinc blende by its peculiar spectrum, viz., the occurrence of two bright lines in the blue and indigo. Formerly the atomic weight of indium was stated as 76, its atomicity as a dyad, and its oxide as InO. A gap, however, was noted by Mendeleef between arsenic and selenium which, under certain circumstances, indium would fill. He therefore assumed its atomic weight to be 114, and In_2O_3 as the oxide, thus bringing it into Series 7, and assigning it a place as an analogue of aluminium. Bunsen has confirmed, from the specific heat of indium, the correctness of Mendeleef's predictions.

Natural History.—Indium is found in zinc blende and in other zinc ores; also in the flue dust of zinc furnaces.

Extraction.—The blende is first acted upon with dilute sulphuric acid in quantity insufficient to effect complete solution. The undissolved residue is then dissolved in nitric acid, and the solution boiled with sulphuric acid until the nitric acid is expelled. Any plumbic sulphate present is now thrown down by adding an excess of water to the solution. The clear filtrate is then treated with an excess of ammonia, and a hydrochloric acid solution of the precipitate (In and Fe) boiled with sodic sulphite. The precipitate thus obtained is a basic indium sulphite. This is dissolved in hydrochloric acid and precipitated with ammonia, the indium hydrate formed being reduced in hydrogen.

The oxide may also be reduced by heating with metallic sodium.

Properties.—Indium is a white or lead-like metal, non-crystalline, soft, and ductile. It is less volatile than zinc or cadmium, but may be distilled. It burns at a red heat with a violet flame, forming the yellow *indium oxide* (In_2O_3). It does not oxidize readily below a red heat. It dissolves in acids. It is very soluble in nitric acid, and slightly soluble both in dilute HCl and H_2SO_4, in the latter case with evolution of hydrogen which, if lighted, will be found to burn with a blue flame. The metal has no action on water, even at its boiling point.

Sulphuretted hydrogen precipitates a yellow-colored *sulphide* (In_2S_3) in neutral solutions, or in solutions containing *acetic acid.* The alkalies and their carbonates give white precipitates.

Compounds of Indium.

COMPOUNDS.	Common Formulæ.	
Indium oxide (yellow oxide)	In_2O_3	A pale yellow powder, prepared by burning the metal in air, or by heating the hydrate or nitrate.
Indium hydrate	$In_2H_6O_6$	Prepared by adding NH_4HO to a solution of an indium salt. A white gelatinous ppt.
Indium chloride .. .. .. [Bromide and iodide analogous to chloride].	In_2Cl_6	
Indium sulphide	In_2S_3	Prepared by direct union at a red heat, or by the action of H_2S on a neutral solution of an indium salt. A yellow powder.
Indium nitrate	$In3NO_3, 4H_2O$	
,, sulphate	$In_2(SO_4)_3, 9H_2O$	
,, sulphite	$2In_2O_3, 3SO_2, 8H_2O$	
,, alum	$In_2(SO_4)_3, (NH_4)_2SO_4, 24H_2O$.	

REACTIONS OF INDIUM COMPOUNDS.

Heated in a Bunsen, indium salts impart a blue color to the flame.

Spectrum. An intense line in the indigo, and also one in the violet.

1. The metal is precipitated from a solution of its salts, by the action of metallic *zinc* or *cadmium.*

2. Boiled with an excess of *acid sodic sulphite,* a precipitate is thrown down of sulphite of indium ($2In_2O_3,3SO_2,8H_2O$).

3. *Sulphuretted hydrogen;* a yellow precipitate (In_2S_3) in neutral solutions, or in solutions containing acetic acid.

4. *Alkaline hydrates and carbonates;* a white precipitate ($In_2H_6O_6$); soluble in excess of ammonic carbonate, or of the fixed alkaline hydrates, but reprecipitated on boiling.

5. *Heated on charcoal,* a ductile metallic bead of the metal may be obtained.

CHAPTER XVI.

GROUP IV.—THE METALS OF THE EARTHS.

ALUMINIUM—GALLIUM—BERYLLIUM—YTTRIUM—ERBIUM—CERIUM—LANTHANUM—DIDYMIUM—THORIUM—ZIRCONIUM—TERBIUM—YTTERBIUM—DECIPIUM—SAMARIUM—SCANDIUM.

ALUMINIUM (Al).

Atomic weight, 27·5. *Specific gravity*, 2·6. *Fuses at* 842° F. (450° C.).
Atomicity pseudo-triad. *Specific heat*, 0·2143.

History.—Discovered by Wöhler, 1828. Obtained in quantity by Deville in 1854.

Natural History.—It is never found free in nature. Next to silica, aluminium, as clay (*silicate of alumina*), is the most abundant of minerals. As an oxide (Al_2O_3), it occurs in corundum, ruby, and sapphire. Although it has been found in certain cryptogamous plants, it can scarcely be regarded as a constituent either of the animal or vegetable kingdoms.

Preparation.—(1.) By decomposing aluminium chloride (Al_2Cl_6) with sodium or potassium (Wöhler).

(2.) By the *electrolysis* of the double chloride of sodium and aluminium ($2NaCl, Al_2Cl_6$). (The double salt is more fusible and less volatile than the simple chloride.)

(3.) (Commercial.) *Bauxite* ($Al_2O_3,Fe_2O_3,2H_2O$), a mineral containing 60 per cent. of Al_2O_3, is heated with soda ash, an aluminate of soda being formed (Na_2O,Al_2O_3). This is dissolved in water, and CO_2 passed through the solution, when alumina is precipitated as a hydrate ($Al_2O_3,3H_2O$). The dried precipitate is now mixed with common salt and carbon, and chlorine passed over the white-hot mixture, a sodium aluminium chloride ($2NaCl,Al_2Cl_6$) distilling over. Upon heating this compound with metallic sodium and cryolite $Al_2F_6,6NaF$), the latter being added as a flux, metallic aluminium s formed, together with sodium chloride.

Properties.—(*a.*) *Physical.* A white, malleable, ductile metal, crysallizing in regular octahedra. Its electric conductivity is about onehird that of silver. It is a very light metal (Sp. gr. 2·5), remarkably sonorous, and slightly magnetic. It melts when heated, but is not volatile.

(β.) *Chemical.* It does not oxidise readily either in steam or in hot or cold air, it being the lightest metal known difficult of oxidation. It does not, when pure and free from sodium, decompose water, even when red-hot. It burns in oxygen (forming Al_2O_3), and in the vapor of sulphur (forming Al_2S_3). Sulphuretted hydrogen is without action upon it; hence its value for ornaments. Nitric acid does not attack it in the cold, and but very slightly even when boiling. Hydrochloric acid, cold or hot, dissolves it freely ($Al_2 + 6HCl = Al_2Cl_6 + 3H_2$). Sulphuric acid and also organic acids in the presence of common salt, dissolve it. Caustic alkalies act energetically upon it, liberating hydrogen. It combines with carbon and with silica. It forms alloys with silver, iron, and copper. "*Aluminum bronze*" is an alloy of copper (90 parts) and aluminium (10 parts), having the color of gold, with twice the tenacity of gun metal. Aluminium does not form an alloy with lead, nor an amalgam with mercury.

Aluminium forms but one oxide, and no carbonate.

Compounds of Aluminium ($Al = 27·5$).

	COMPOUNDS.	Formulæ (Common).	Molecular Weight of Anhydrous Compound.	Specific Gravity (Crystal).
1	Aluminium oxide (alumina) ..	Al_2O_3	103	3·95
2	,, chloride	Al_2Cl_6	268	
3	,, bromide	Al_2Br_6	535	
4	,, iodide	Al_2I_6	817	
5	,, fluoride	Al_2F_6		
6	,, sulphide	Al_2S_3	151	1·671
7	,, sulphate	$Al_23SO_4,18H_2O$	343+324	
8	,, potassic sulphate (alum)	$K_2Al_24SO_4,24H_2O$	517+432	1·726
9	,, nitrate	$Al_26NO_318H_2O$	427+324	
10	,, phosphate	$Al_2(PO_4)_2$	245	
11	,, silicates			
	Potash alum			
	Ammonia alum			
	Soda alum			

(1.) **Aluminium Oxide.**—*Alumina* (Al_2O_3). This is the only oxide of aluminium. It occurs native as "corundum" (the next hardest body to the diamond), as "emery," as the "ruby" (colored with a chromium salt), as "sapphire" (probably colored with cobalt), as the "spinelle" (MgO,Al_2O_3), and as "topaz" (a compound of alumina, silica, and aluminium fluoride). *Hydrargillite*, *Bauxite*, *Diaspore* (Al_2O_3, H_2O) and *Gibbsite* ($Al_2O_3,3H_2O$) are native hydrates. "*Emery*" is alumina mixed with sand and iron.

Preparation.—(1.) (As a hydrate, $Al_2O_3,3H_2O=Al_2H_6O_6$.) By adding ammonia to an alum solution.

(2.) (As amorphous Al_2O_3.) By the ignition of the hydrate or of ammonia alum.

(3.) (As crystalline Al_2O_3.) By the action, at a high temperature, of boric anhydride on aluminium fluoride, or by heating a mixture of barium fluoride and alumina.

Artificial gems have been formed by heating a mixture of alumina and red lead, whereby a crystalline alumina is formed, which, with 2 or 3 per cent. of potassium bichromate and barium fluoride give ruby crystals, and with cobaltous oxide crystals of a sapphire tint.

Properties.—The hydrate when first precipitated is a bulky transparent gelatinous precipitate, contracting when dried at ordinary temperatures to a gummy hygroscopic mass ($Al_2H_6O_6,2H_2O$). This compound on ignition at 572° F. (300° C.) becomes Al_2O_3,H_2O. It absorbs a large quantity of heat in losing water, on account of which property it is used for filling the space between the iron plates of fireproof safes. The hydrate ($Al_2H_6O_6$), is very soluble in acids as well as in solutions of the caustic alkalies, but the anhydrous oxide (Al_2O_3), is almost insoluble in acids as well as in alkalies. Alumina fuses at the heat of the oxyhydrogen blowpipe, forming a colorless, transparent mass.

When freshly precipitated, the hydrate dissolves in a solution of aluminium chloride, from which the hydrochloric acid may be dialysed out, colloidal alumina ($Al_2H_6O_6$) remaining on the dialyser in solution. This solution of colloidal alumina, like that of dialysed iron (p. 406), is very unstable, for if it be allowed to remain exposed to air, coagulation slowly occurs, such change being immediate on the addition of an acid, an alkali or a salt, to the solution.

Alumina is capable of acting both as a base and as an acid. Thus, as a feeble *base* it forms salts with acids (*e.g.*, aluminic sulphate, $Al_2O_3,3SO_3$). These salts have an acid reaction, and are easily decomposed. As a feeble *acid* it combines by fusion with basic oxides, forming a class of soluble salts known as "*the aluminates*" (*e.g.*, sodium aluminate, Na_2O,Al_2O_3). Thus the *spinelle ruby* is a magnesium aluminate (MgO,Al_2O_3), *gahnite* a zinc aluminate (ZnO,Al_2O_3), *chrysoberyl* a beryllium aluminate (BeO,Al_2O_3). A potassium aluminate has also been obtained (K_2O,Al_2O_3).

Alumina combines with silica to form clay.

Aluminium hydrate combines with certain organic coloring matters, forming a class of pigments called "*lakes.*" Thus alum is used as a *mordant* to fix coloring matters on fibres having no direct affinity for such coloring matters.

(2.) **Aluminium Chloride.**—(Al_2Cl_6). Specific gravity of vapor, 9·27.

Preparation.—(1.) By passing chlorine over a mixture of carbon and alumina heated to redness ($Al_2O_3+C_3+3Cl_2 = Al_2Cl_6+3CO$).

(2.) By heating clay in a mixture of hydrochloric acid gas and the vapor of carbon disulphide.

[NOTE.—Aluminium chloride cannot be prepared by dissolving Al_2O_3 in HCl, and evaporating the solution to dryness. A hydrate of aluminium chloride ($Al_2Cl_6,12H_2O$) is no doubt formed in the solution, but this on evaporation evolves HCl, leaving a residue of Al_2O_3.]

Properties.—A white (colored only if it contains impurities), crystalline, deliquescent body, emitting fumes of HCl when exposed to the air. It is soluble in alcohol, and dissolves with a hissing noise when placed in water. It sublimes before melting, but may be fused under the pressure of its own vapor. It combines with ammonia, with phosphoretted hydrogen, and with sulphuretted hydrogen. It forms compound chlorides when heated with the chlorides of other elements (*e.g.*, $Al_2Cl_6,2KCl$).

"*Chloralum*" is an impure aluminium chloride.

The *Sulphide, Bromide, and Iodide of Aluminium* may severally be formed by direct union.

(5.) **Aluminium Fluoride** (Al_2F_6) is found native as *cryolite* ($6NaF,Al_2F_6$), and as *topaz*, [$2(Al_2O_3,SiO_2),Al_2O_3SiF_4$].

(7.) **Aluminium Sulphate** ($Al_23SO_4,18H_2O$) may be obtained by dissolving alumina in sulphuric acid. It is prepared commercially by dissolving aluminium hydrate, obtained from cryolite or bauxite (taking care the mineral is free from iron), in sulphuric acid, or by boiling china clay (hydrated aluminium silicate) with sulphuric acid. The clear solution thus obtained, having been freed from iron by potassic ferrocyanide and evaporated to a syrup, is known to the dyers (by whom it is used as a mordant) and to the paper-makers (by whom it is used for weighting purposes), as "*concentrated alum*," or when reduced to the solid state as "*cake alum*." The crystals are exceedingly soluble in water (1 in 2 parts by weight). Basic sulphates have been prepared by boiling aluminium sulphate with the freshly-prepared hydrate.

THE ALUMS.

These are double sulphates, *i.e.*, sulphate of alumina with a sulphate of potash (forming potash alum), or of ammonia (forming ammonia alum), of soda, of thallium, of silver, etc. The alumina is the valuable ingredient in commercial alums.

But the term "*alums*" designates a class, rather than bodies containing aluminium or its compounds. Thus in potash alum, which has the formula $K_2Al_24SO_4$, not only may the K_2 be replaced by Na_2, or by $(NH_4)_2$, etc., but the Al_2 may also be replaced by such groups as Cr_2, or by Fe_2, or by Mn_2, etc. Thus we speak of *chrome alum* (K_2Cr_2

$4SO_4$), although the compound contains no aluminium. The alums contain two metals, therefore, either of which may be replaced by isomorphous metals, yielding compounds analogous to common alum, and crystallizing in similar forms. Further, the alums need not be sulphates. Thus, selenic acid forms a series of alums, of which $K_2Al_24SeO_4,24H_2O$ is an illustration.

(8.) **Potassium Aluminium Sulphate.**—*Potash or Common Alum* ($K_2Al_24SO_4,24H_2O$).

Natural History.—Found native in volcanic districts, produced by the action of volcanic sulphuric acid on the aluminium compounds of the rocks.

Preparation.—(1.) (*a.*) "Alum shale" (a compound of aluminium silicate, iron disulphide, and bituminous matters) is first roasted, whereby one-half of the sulphur of the FeS_2 becomes oxidized. The residue, after being moistened with water, is exposed to the air, ferrous and ferric sulphates with free sulphuric acid being formed.

(*β.*) The free sulphuric acid formed decomposes the aluminium silicate, forming aluminium sulphate.

(*γ.*) When the mass is lixiviated with water, a solution results (called crude alum liquor), containing aluminium sulphate, ferrous and ferric sulphates, and probably more or less magnesium sulphate.

(*δ.*) The greater part of the ferrous sulphate (the presence of which is undesirable), is now removed by crystallization.

(*ε.*) Potassium chloride (in the form of soapboilers' waste, or the refuse of glasshouses or of saltpetre refineries) is now added to the solution, whereby any ferric sulphate is decomposed, a soluble ferric chloride, together with potassium sulphate, resulting :—

$$\underset{\text{Potassic chloride}}{6KCl} + \underset{\text{Ferric sulphate}}{Fe_23SO_4} = \underset{\text{Ferric chloride}}{Fe_2Cl_6} + \underset{\text{Potassic sulphate.}}{3K_2SO_4}$$

(*ζ.*) The potassium sulphate as soon as formed, combines with the aluminium sulphate to form "*potash alum*," which being sparingly soluble in cold water is deposited from the solution as "alum meal" or "alum flour." This is afterwards washed with cold water to remove adherent iron, and crystallized.

Very frequently *ammonium sulphate* (from gas liquor) is used instead of potassium chloride (ε), in which case an *ammonia alum* is formed, $(NH_4)_2Al_24SO_4,24H_2O$.

If *sodium sulphate* be employed, *soda alum* is formed ($Na_2Al_24SO_4$ $24H_2O$). Thus we may obtain by the employment of different reagents a series of alums, some which may be tabulated as follows :—

Potash alum	$K_2Al_24SO_4,24H_2O$.
Soda alum	$Na_2Al_24SO_4,24H_2O$.
Ammonia alum...	$(H_4N)_2Al_24SO_4,24H_2O$.

Iron alum	$K_2Fe_24SO_4,24H_2O$.
Chrome alum	$K_2Cr_24SO_4,24H_2O$.
Manganese alum	$K_2Mn_24SO_4,24H_2O$.

Further, a silver-alum, a cæsium-alum, and a thallium-alum may be obtained.

(2.) Potash alum may also be prepared by burning "*alum stone*" (*alumite*, a native basic sulphate of alumina and potash, found in Hungary and Italy), exposing the roasted mass to the air, and finally extracting with water. The water dissolves out the alum from the mass, and leaves the insoluble alumina :—

$$\begin{array}{ccccc} K_2SO_4,3Al_2SO_6,6H_2O & = & 2(Al_2O_3,3H_2O) & + & K_2Al_24SO_4 \\ \text{Alum stone} & = & \text{Alumina} & + & \text{Alum.} \end{array}$$

The alum thus prepared is known as "*Roman alum.*"

(3.) Also by mixing sulphate of alumina with sulphate of potassium in proper proportions.

Properties.—Alum is a white, crystalline (cubes or octahedra), astringent-tasted body, soluble in water (1 in 18 aq., at 60° F., and 1 in 1 at 212° F.) ; insoluble in alcohol. It is but little affected by exposure to air. Its solution has an acid reaction, and dissolves iron and zinc with the evolution of hydrogen. When alum is first heated, it melts in its own water of crystallization. At 392° F. (200° C.) the water evaporates, and the residue swells up to a white, infusible and insoluble mass called *burnt alum* ($K_2Al_24SO_4$). By ignition, some of the acid of this alum may be expelled. *Homberg's pyrophorus* is a mixture of alum and sugar, carbonized out of contact with air.

Alum is largely used in dyeing, in the preparation of skins, in medicine, etc.

We have in the *alums* a marked illustration of isomorphism, that is, of bodies having different chemical composition crystallizing in the same form. The colors of the alums are very varied: thus, *Potash alum* forms white octahedra ; *chrome alum*, dark red octahedra ; *iron alum*, violet octahedra, etc.

(10.) **Aluminium Phosphates** are found as natural minerals, as, *e.g.*, *turquoise*, which is a hydrated phosphate, colored with copper and iron ($2Al_2O_3,P_2O_5,5H_2O$) ; *wavellite*, $3(4Al_2O_3,3P_2O_5,18H_2O)$, Al_2F_6 ; *lazulite* (a double phosphate, colored with phosphate of iron), etc. The phosphate $Al_2P_2O_8$ is obtained as a gelatinous precipitate on adding sodium phosphate to a solution of an aluminium salt. It is insoluble both in ammonia and in acetic acid, but is soluble in alkalies and in acids generally.

(11.) **Aluminium Silicates.**—These are both numerous and complicated. Their complication arises from the frequent replacement of Al_2O_3 by the isomorphous body Fe_2O_3, other metals present being similarly exchanged for their isomorphous representatives.

A few of these silicates are stated in the following table :—

	Garnet (Ca, Al, Mg, Fe and Mn)		$3(CaMgFoMn)O(AlFe)_2 3SiO_2$
	Chlorite (Al, Mg, etc.)		$4(MgFe)O,(AlFe)_2O_3,2SiO_2,3H_2O$
	Basalt (Ca, Mg)		$4(CaMgFe)O5SiO$
	Cyanite, Diothene		Al_2O_3,SiO_2
Zeolites	Analcime (Na, Al)		$Na_2O,Al_2O_3,4SiO_2,2H_2O$
	Stilbite (Ca, Al)		$CaO,Al_2O_3,6SiO_2,6H_2O$
	Prehnite (Ca, Al)		$CaO,Al_2O_3,3SiO_2,H_2O$
Felspars	Potash * Felspar (orthoclase)	K_2	$O,Al_2O_3,6SiO_2$
	Sodium ,, (albite)	Na_2	
	Lithium ,, (petalite)	L_2	
	Calcium ,, (Labradorite)	Ca	
Mica	Uniaxial (Mg and Al)		$[4(MgKFe)O,(AlFe)_2O_3,4SiO_2]$
	Biaxial K in excess		$\left[\left(\begin{matrix}K\\Li\end{matrix}\;Fe\right)O,3(AlFe)_2O_3,6SiO_2\right]$
	Biaxial Li in excess (Lepidolite)		

Slate is an aluminium silicate of varied composition. *Roofing slate* is an argillaceous rock; *mica slate* contains mica, and *hornblende slate*, hornblende. *Granite* and *gneiss* consist of quartz, felspar and mica; *porphyry* is a felspar, so also is *basalt*, the latter containing crystals of augite. *Dolerite*, *greenstone*, *diorite*, *trachyte*, *fuller's earth*, *pumice stone*, (which, in a melted state, is called *volcanic glass* or *obsidian*), are also aluminic silicates.

Lapis lazuli (*native ultramarine*) consists of a silicate of alumina mixed with lime, soda, sulphuric acid, sulphur and iron. The cause of its blue color is not well understood.

Artificial ultramarine is prepared by heating together a mixture of 100 parts of kaolin, 100 of sodium carbonate, 160 of sulphur, and 12 of carbon. A sodium sulphide is formed, which combines with the aluminium silicate. A green body used as a pigment results (*green ultramarine*). This, on being roasted with fresh sulphur, forms a brilliant blue mass (*blue ultramarine*). Ultramarine is bleached by acids with evolution of sulphuretted hydrogen, and also by chlorine. With hydrochloric acid, H_2S is evolved, and amorphous silicic acid set free. It is often used as a coloring matter for oil paint and for blue paper, which consequently becomes white when dipped in an acid.

Clay.

Formation.—The disintegration of granite rocks, which consist of quartz, felspar and mica, results both from mechanical and chemical agencies. By the action of air, and by the expansion of the water in the rock during congelation, it is gradually broken down. From this debris, water containing carbonic acid dissolves out the potash, leaving quartz and silicate of alumina. These bodies, owing to their different gravities, are afterwards mechanically separated by the action of water, the silicate of alumina being comparatively light. This, when deposited, constitutes *clay* ($Al_2O_3.2SiO_2,2H_2O$).

Composition of clay.—The composition of clays varies considerably, as the following diagram shows:—

* *Pericline* is an admixture of potash and soda felspar.

	Washed Kaolin.			Stourbridge Fire Clay.	Pipe Clay.	Sandy Clay.	Blue Clay.	Brick Clay.
	Chinese.	S. Yrieix.	Cornish.					
Silica	50·5	48·37	46·32	64·10	53·66	66·68	46·38	49·44
Alumina ..	33·7	34·95	39·74	23·15	32·00	26·08	38·04	34·26
Oxide of iron..	1·8	1·26	0·27	1·85	1·35	1·26	1·04	7·74
Lime	—	—	0·36	—	0·40	0·84	1·20	1·48
Magnesia ..	0·8	trace	0·44	0·95	trace	trace	trace.	5·14
Potash or soda	1·9	2·40	12·67					
Water	11·2	12·62		10·00	12·08	5·14	13·57	1·94
	99·9	99·60	99·80	100·05	99·49	100·00	100·23	100·00

From MILLER.

Loam is a clay containing ferric oxide, whilst *marl* is a clay containing carbonate of lime. *Umber*, *red-bole*, *ochre* and *sienna*, are also clays containing various iron and manganese oxides.

Properties.—A tenacious mass, insoluble in, but capable of diffusion through water, very plastic, but shrinking when dried. It has a characteristic odor, and possesses great absorbent powers. It consequently retains the ammonia from manure when placed on the earth, storing it up for the vital functions of the plant. It also purifies water impregnated with organic impurities when passed through it. (Way.)

Clay is decomposed by sulphuric acid (*see* Preparation of Alum), but is very slowly acted upon by hydrochloric or by nitric acid. After clay has been ignited, no acid, except hydrofluoric acid, has the least action upon it. It is slightly soluble in a solution of caustic potash, but becomes very soluble in water after fusion with potassic hydrate.

Porcelain and Pottery.

Clay is employed in the manufacture of all kinds of pottery. Although plastic, it shrinks considerably when baked, to prevent which, sand, chalk, or bone-ash is mixed with the clay. But inasmuch as these bodies have a tendency to disintegrate the clay, it is necessary after baking to glaze the article with some substance capable of vitrification, in order to cement the whole together and form it into a compact mass. Upon this principle depends the manufacture of pottery.

(1.) *Bricks, coarse tiles, pipes*, etc., are made from common clay, of which there are three kinds, (*a*.) *marly or chalky clay* *, used for pale bricks ; (*β*.) *potter's clay*, used for bricks and tiles ; (*γ*.) *fire clay*, which is nearly free from lime.

---

* A marl is a clay containing a considerable quantity of calcic carbonate. If the alumina be in excess, it is an *aluminous marl*, if the chalk, a *calcareous marl*.

Process.—The clay is dug up in the autumn, and exposed to the air for a considerable time (weathered). The stones present in the clay are either crushed in a mill or removed by puddling. This done, the clay is mixed with sand and well kneaded. The mass is then ready to be fashioned into shape by hand or machinery, the articles so formed being first dried in the air, afterwards fired in kilns, and finally glazed with a mixture of clay and litharge, iron scarf, etc.

The red color of bricks and tiles is due to the carbonate of iron present in common clay becoming converted into peroxide (Fe_2O_3).

(2.) *Common earthenware.*—One of three kinds of clay is employed in the manufacture of common earthenware, *viz.*, (α) *Dorsetshire clay*, (β) *Devonshire clay* (blue clay), and (γ) *pipe clay.*

The clay is first of all cleansed by machinery, and reduced to a state of pap. It is then run through fine sieves. To prevent after-contraction and unequal drying, the clay thus prepared is mixed with a pap of ground flints. This flint-pap is prepared by subjecting flints from the chalk to an intense heat, suddenly quenching them with water, and finally grinding. The mixed mass of sand and clay, called "*slip*" (1 part of flints to 5 parts of clay), is now cut into square blocks, and kept for some months in a damp place. In this way any organic matter present becomes oxidized, the sulphates being reduced to sulphides. When required, the "slip" is kneaded by beating on a board, so as to effect perfect incorporation, and the removal of air bubbles. This kneading process in England is effected both by machinery and by hand labor. In France it is done with mallets; in Egypt by the treading of men; and in China by the treading of cattle. The article, after being roughly fashioned, is partially dried at a temperature varying from 80° to 90° F. It is then baked in kilns, and placed in cases called "saggars." This material has the appearance of a porous earthenware, and is known as "biscuit." The freshly-struck pattern, printed on wet soaped paper with a mixture of some metallic oxide and boiled oil, is now placed on the "biscuit," and well rubbed in with a flannel rubber, so that the "biscuit" may completely remove the printed impression from the paper. As soon as the design is absorbed by the "biscuit," the paper is removed by wetting with a sponge. The "biscuit" is now dipped into a weak alkaline lye, in order to saponify the oil, and afterwards glazed with some fusible material, such as a mixture of white lead, Cornish stone, ground flints, ground glass, chalk felspar, silicate of alumina and potash, or borax. It is inally baked or "fired" in a kiln, whereby the glaze is fused.

The colors on the earthenware are produced by various metallic oxides (*see* page 364), which form a colored glass with the glaze, whilst the metallic lustres are produced by gold, platinum, copper, brass, etc.

(3.) *Porcelain* (china) is a finer variety of pottery. It is of two kinds; (α.) The *hard* porcelain, such as is made at Sèvres, Dresden, etc., is manufactured from *kaolin,* a very pure white clay, obtained from China, Cornwall, S. Yricix near Limoges, etc., and from *china stone,* which consists of the silicates of alumina, potash and lime. The glaze used is a mixture of felspar and quartz, suspended in water, into which the article is dipped. (β.) The *soft* variety of porcelain, as made in England, consists of kaolin mixed with bone earth and borax. After baking (*biscuit*), its further treatment corresponds to the description already given.

Wedgwood is a fine description of stoneware.

Salt Glazing, which is largely used in the preparation of stoneware, etc., is effected by throwing common salt into the furnace containing the heated articles, which have been previously dipped into a mixture of sand and water. The salt volatilizes, and is decomposed by the sand on the hot surface of the ware. A fusible impervious silicate is thus formed as a glaze, hydrochloric acid escaping as vapor with the excess of salt ($H_2O + 2NaCl + SiO_2 = 2HCl + Na_2O,SiO_2$).

REACTIONS OF ALUMINIUM COMPOUNDS.

Non-luminous flame. No action.

Salts. Colorless (if the acid be colorless), sweet, and astringent. Acid to litmus.

Caustic alkalies, and *ammonium carbonate*, *hydrate* or *sulphide.*—A white ppt. of $Al_2H_6O_6$. Soluble in excess of caustic alkalies, but scarcely at all soluble in ammonia.

Blow-pipe.—Moistened with cobaltous nitrate and ignited, aluminium compounds yield a pale blue mass (Thénard's blue).

GALLIUM (Ga).

Atomic weight, 69·5. *Atomicity, pseudo-triad.* *Fuses at* 86·27° F. (30·15° C.). *Specific gravity,* 5·9. *Specific heat,* 0·080.

History.—Discovered, by means of the spectroscope, by Lecoq de Boisbaudran (1875). Termed gallium from Gallia (France).

Occurrence.—It occurs associated with zinc in the zinc blende of Bensberg; also in the yellow transparent blende of the Asturias, and in the brown blende of Pierrefitte (0·0016 per cent.). Zinc dross and the Swedish brown blende contain sensible traces of gallium.

Preparation.—By the electrolysis of a solution of the oxide in potassic hydrate, or of an alkaline solution of the sulphate.

Its separation from zinc is effected by fractional precipitation with sodium carbonate, the carbonate of gallium going down before the carbonate of zinc.

Properties.—A silvery white metal. Specific gravity 5·9. It fuses when placed in the warm hand [86° F., 30·0° C.]. It continues in this "superfused" state for several days even when cooled to 32° F. (0° C.), provided it is carefully protected and allowed to remain at rest. If any part of its surface, however, comes into contact with a trace of solid gallium, a solid spot is seen to form, which rapidly spreads until the entire mass solidifies. On crystallising, the metal assumes a bluish tint, and its lustre diminishes. The solid metal may be cut with a knife, and is both flexible and malleable. Heated to bright redness in the presence of air, gallium does not volatilize, but merely oxidizes superficially. When cold, the metal has only to be rubbed with a rod to restore its original brightness. It dissolves in HCl, and in KHO with evolution of hydrogen. Hot nitric acid dissolves it, but not the cold acid.

Gallium Oxide (Ga_2O_3), a white substance, insoluble in water, soluble in caustic alkalies and ammonia.

Gallium Chloride (Ga_2Cl_6) is a deliquescent substance, soluble in a little water, but decomposed by an excess of water, with the formation of an oxychloride.

Gallium Sulphate (Ga_23SO_4) is a non-deliquescent substance, and very soluble in water. It forms a *gallium alum*, $(NH_4)_2Ga_24SO_4, 24H_2O$.

REACTIONS OF GALLIUM.

Spectrum (spark) two lines in the violet.

BERYLLIUM (Glucinum) (Be).

Atomic weight, 9·4. *Specific gravity*, 2·1. *Specific heat*, 0·408.
Atomicity, dyad.

[NOTE.—The symbol G has also been given to this element.]

History.—Isolated by Wöhler in 1828. (Βήρυλλος, *beryl.*)

Natural History.—Occurs combined with silica in *phenacite* ($BeSiO_4$), with silica and alumina in the *emerald*, in the *aquamarine*, and in the *beryl* $[3(BeO)Al_2O_33(SiO_2)]$ colored with chromium ; also also in the *chryso-beryl.*

Preparation.—By passing the vapor of beryllium chloride mixed with hydrogen over heated sodium. The metal may be prepared by a process similar to that described for the preparation of aluminium (p. 437).

Properties.—A white, fusible, malleable metal. Specific gravity 2·1. It does not burn in air, oxygen, or in sulphur vapor, but it combines readily with chlorine, iodine, and silicon. It does not decompose steam. It is soluble in dilute warm sulphuric acid, and in dilute cold hydrochloric acid with evolution of hydrogen, but is insoluble in nitric acid. It is not soluble in ammonia, but is dissolved, with the evolution of hydrogen, by a solution of potash. Its salts are colorless, sweet (γλυκὺς, hence the name *glucinum*), and acid to litmus.

Compounds of Beryllium.

1.	Beryllium oxide	BeO.
2.	,, hydrate	BeH_2O_2.
3.	,, chloride	$BeCl_2$.
4.	,, bromide	$BeBr_2$.
5.	,, iodide	BeI_2.
6.	,, nitrate	$Be2NO_3,3H_2O$.
7.	,, carbonate	$BeCO_3,4H_2O$.
8.	,, sulphate	$BeSO_4,7H_2O$.
9.	,, phosphates	$BeHPO_4,3H_2O$; $Be(NH_4)_2Na_22PO_4,7H_2O$.
10.	,, silicate	$2BeOSiO_2(2BeO,SiO_2)$.
11.	,, sulphide	BeS.

(1.) **Beryllium Oxide** (*Beryllia*, BeO). *Preparation.*—From the Beryl. By igniting the carbonate or hydrate. *Properties.*—A white powder like magnesia. Specific gravity, 3·08. Insoluble in water, and, after ignition, insoluble in dilute acids.

(2.) **Beryllium Hydrate** (BeH_2O_2). *Preparation.*—By adding ammonia to a solution of a beryllium salt. *Properties.*—A gelatinous precipitate, which, when dried, becomes a white powder, and by ignition is converted into BeO. Soluble in caustic soda and potash. It is also soluble in ammonium carbonate, a basic carbonate separating when the solution is boiled. Insoluble in ammonia.

(3.) **Beryllium Chloride** ($BeCl_2$). *Preparation.*—By passing chlorine over a mixture of charcoal and beryllium oxide. A solution of $BeCl_2$ may be prepared by dissolving the oxide in HCl. *Properties.*—A crystalline, deliquescent, fusible, and volatile compound.

(7.) **Beryllium Carbonate.** *Preparation of a basic salt.*—By adding an alkaline carbonate to a solution of a beryllium salt. *Properties.*—The basic salt is soluble in water containing CO_2. If the solution be evaporated over H_2SO_4 in an atmosphere of CO_2, it yields the normal salt ($BeCO_3,4H_2O$), which, on exposure to air, again becomes a basic salt.

(8.) **Beryllium Sulphate** ($BeSO_4,7H_2O$).–The anhydrous sulphate may be obtained by heating the crystals. BeO is formed when the salt is ignited. The sulphate forms double compounds with potassium and magnesium sulphates.

(11.) **Beryllium Sulphide** (BeS) is prepared by heating the metal in sulphur vapor. (Alkaline sulphides precipitate BeH_2O_2 from solutions of beryllium salts.)

Reactions of Beryllium Compounds.

Flame.—No color imparted to a non-luminous flame.

Spectrum.—Two characteristic lines in the blue.

Alkaline hydrates, ammonia and ammonium sulphide.—A white gelatinous ppt. of BeH_2O_2, soluble in excess of caustic alkalies, but not in excess of ammonia.

Carbonate of ammonia (solution) dissolves BeH_2O_2, in which respect it differs from alumina, and by which reaction its separation from alumina may be effected.

THORIUM (THORINUM) ($Th = 231{\cdot}4$). *Specific gravity*, 7·8. *Atomicity, tetrad.*

Thorium was discovered by Berzelius (1829) in the mineral thorite (thorium silicate), and may be prepared by reducing the chloride with potassium. The metal is a grey powder, incapable of decomposing water, but combustible in air, forming its only oxide thoria (ThO_2), a body isomorphous with SnO_2 and TiO_2 (Sp. gr. = 9·4). It is not acted on by the caustic alkalies, but is soluble in most acids. Thorium chloride ($ThCl_4$) and fluoride have also been prepared.

ZIRCONIUM ($Zr = 90$). *Specific gravity*, 4·15. *Atomicity* ^{iv} ($ZrCl_4$).

Zirconium is found in nature as an oxide (zirconia, ZrO_2) and as a silicate in the rare minerals, zircon and hyacinth (ZrO_2SiO_2).

Preparation.—By heating zirconium potassic fluoride (ZrF_4,KF_2) with potassium or aluminium, or the chloride ($ZnCl_4$) with sodium, etc.

Properties.—Like silicium, to which it is closely allied, it exists in three states—(1,) *amorphous*, which burns when heated in the air below redness, forming *zirconia* (ZrO_2); (2,) *crystalline*, a body requiring the oxy-hydrogen flame to fire it; and (3,) *graphoidal.*

Zirconium has never been fused. It decomposes water slowly at the boiling point. It is acted on by hydrofluoric acid with the evolution of hydrogen, and also by aqua regia. It is insoluble in dilute sulphuric and hydrochloric acids.

It forms one oxide, *zirconia* ($ZrO_2 = 122$; Specific gravity, 4·5), a white infusible powder, which, unlike alumina, is insoluble in the caustic alkalies. It is insoluble in strong sulphuric acid, but soluble in potassic carbonate. It acts both as a base and as a feeble acid, in the latter case forming compounds called *zirconates.* Sodium zirconate (Na_2ZrO_3) is formed by fusing zirconia with an alkaline carbonate, when CO_2 is driven off. A zirconium hydrate (ZrH_4O_4) is formed when an alkaline zirconate is treated with water, or when ammonia is added to a solution of a zirconium salt.

Zirconium chloride ($ZrCl_4 = 231{\cdot}5$), *bromide* ($ZrBr_4$), and *fluoride* (ZrF_4) have been prepared. *Zirconium fluoride* forms, by its combination with metallic fluorides, a class of compounds known as the zircono-fluorides.

CERIUM ($Ce = 140{\cdot}5$). *Atomicity, tetrad; pseudo-triad* (CeO_2; Ce_2Cl_6).

History.—Discovered by Klaproth, 1803.

Natural History.—Found as a silicate, in conjunction with lanthanum and didymium, in cerite; also as a phosphate in monazite, and as a fluoride in fluocerite.

Preparation.—By the electrolysis of the fused chloride.

Properties.—A malleable, ductile, dark-colored metal. Tarnishes in moist air. Burns in air brilliantly. Sp. gr. 6·7. Decomposes water slowly. It is dissolved both by HCl and dilute H_2SO_4, hydrogen being evolved. Insoluble in strong sulphuric and nitric acids.

Cerium oxalate is given in medicine for the relief of the sickness of pregnancy.

COMPOUNDS OF CERIUM.

Cerous chloride	Ce_2Cl_6.
[Analogous compounds with bromine, iodine and fluorine.]	
Cerous oxide	Ce_2O_3.
„ nitrate	$Ce_26NO_3,12H_2O$.
„ sulphate	$Ce_23SO_4,9H_2O$.
„ phosphate (*monazite*) ...	$Ce_2P_2O_8$.
Ceric fluoride	CeF_4.
„ oxide	CeO_2.
„ nitrate	$Ce4NO_3$.
„ sulphate	$Ce2SO_4,7H_2O$.

DIDYMIUM (Di = 146). *Molecular weight* (?). *Atomicity, triad and pentad.*

History.—Discovered by Mosander (1841).

Natural History.—Found in cerite. (*See* Cerium.)

Preparation.—Separated, together with lanthanum, from cerium, as an oxalate, and further separated from lanthanum by the fractional precipitation of the sulphates.

Properties.—A yellowish metal. Sp. gr. 6·54.

COMPOUNDS OF DIDYMIUM.

Didymous chloride	$DiCl_3$.
„ oxide	Di_2O_3.
„ hydrate	DiH_3O_3.
„ nitrate	$Di3NO_3,6H_2O$.
„ sulphate	$Di_33SO_4,8H_2O$.
Didymic oxide	Di_2O_5.

Recent researches have clearly demonstrated the compound nature of didymium. Wilsbach has shown that by repeated crystallizations, a didymium salt can be separated into two new elements, which he termed *neodymium*, the salts of which are of an amethyst color, and *praseodymium*, the salts of which are green. He fixes 143·6 as the atomic weight of praseodymium, and 140·8 as the atomic weight of neodymium. (*Journal of Chemical Society*, XLVIII. (1885), p. 1113. See also *Chemical Society's Journal*, Vol. XLIII., p. 281.)

YTTRIUM (Y = 89·8). *Molecular weight* (?). *Atomicity, triad.*

History.—Yttrium was discovered by Gadolin (1794).

Natural History.—Widely diffused (Crookes). Occurs in certain rare minerals with erbium. Found in conjunction with cerium, lanthanum, didymium, beryllium, etc., in gadolinite.

COMPOUNDS OF YTTRIUM.

Yttrous chloride	YCl_3.
" oxide (yttria)	Y_2O_3.
" nitrate	$Y3NO_3,6H_2O$.
" sulphate	$Y_23SO_4,8H_2O$.

The remarkable researches of Crookes have indicated beyond doubt that yttrium is a compound of several new metals—certainly five, and probably eight. This is about all we are able to say at present. Their individual separation has been effected by a process of fractional precipitation. (See *Chemical News*, Sept. 24, 1886, p. 155.)

ERBIUM (Er 165·9). *Molecular weight* (?). *Atomicity triad.*

History.—Discovered by Mosander (1843).

COMPOUNDS.

In all respects analogous to yttrium.

TERBIUM (Tr 148·8 ?).

Occurs with yttrium and erbium in samarskite.

YTTERBIUM (Yb = 172·8).

A supposed new metal. Discovered by Marignac in crude erbia.

SCANDIUM (Sc = 44).

Discovered by Nilson (1879) in gadolinite. Forms an oxide of the composition Sc_2O_3.

SAMARIUM (Sm = 150).

Discovered by Lecoq de Boisbaudran in samarskite by its peculiar spectrum.

Compounds resemble didymium.

DECIPIUM (Dp = 159 ?).

Discovered by Delafontaine in samarskite by its special absorption spectrum.

NORWEGIUM ($Ng = 214$?).

Discovered by Dahll in a specimen of Norwegian nickel glance. Sp. gr. 9·44. Fuses at 489° F. (254° C.). Chemically, it is said to resemble bismuth.

LANTHANUM ($La = 138{\cdot}5$). *Molecular weight* (?). *Atomicity, triad* ($LaCl_3$).

History.—Discovered by Mosander (1839).

Natural History and Preparation.—(*See* Cerium and Didymium.)

Properties.—An iron-grey metal, quickly tarnishing on exposure. Sp. gr. 6·136.

Compounds of Lanthanum.

Lanthanous chloride	$LaCl_3$.
„ oxide	La_2O_3.
„ hydrate	LaH_2O_3.
„ nitrate	$La3NO_3,6H_2O$.
„ sulphate	$La_23SO_4,9H_2O$.

The anhydrous sulphate is soluble in ice-cold water.

CHAPTER XVII.

METALS OF GROUP III.

A.—METALS WHOSE SULPHIDES ARE INSOLUBLE IN THE ALKALINE SULPHIDES.

COPPER and its Compounds—BISMUTH and its Compounds—CADMIUM and its Compounds—PALLADIUM and its Compounds—RHODIUM and its Compounds—OSMIUM and its Compounds—RUTHENIUM and its Compounds.

B.—METALS WHOSE SULPHIDES ARE SOLUBLE IN THE ALKALINE SULPHIDES.

TIN and its Compounds—TITANIUM and its Compounds—ANTIMONY and its Compounds—ARSENIC and its Compounds—GOLD and its Compounds—PLATINUM and its Compounds—Bases produced by the action of Ammonia on the Chlorides of Platinum—MOLYBDENUM and its Compounds—IRIDIUM and its Compounds.

COPPER ($Cu'' = 63 \cdot 5$).

Atomic and Molecular weight, 63·5. *Specific gravity*, 8·9. *Specific heat*, 0·0935. *Fuses at* 2426° F. (1330° C.). *Atomicity, dyad in cupric salts* ($Cu''Cl_2$) ; *pseudo-monad* (*the double atom of* Cu_2 *acting as a dyad*) *in cuprous salts* ($'Cu'_2Cl_2$).

History.—Known to the ancients.

Natural History.—Copper is found native both in masses and in crystals, not unfrequently associated with silver. The common copper ores are, a sulphide of copper and iron called "*copper pyrites*" or "*yellow copper ore*" (Cu_2S,Fe_2S_3), a cuprous sulphide or "*copper glance*" (Cu_2S), and cupric sulphide or "*indigo copper*" cuprous arsenide (Cu_6As_2), cuprous oxide or "*red copper ore*," or "*ruby ore*" (Cu_2O). Copper is also found as cupric oxide, *tenorite* or "*black oxide*" (CuO), and as *malachite*, the green malachite having the composition represented by the formula ($CuCO_3.CuO,H_2O$), and the blue malachite or *azurite* by the formula ($2CuCO_3,CuO,H_2O$). The metal is also found in seaweed and in the blue blood (hæmocyanin, the analogue of hæmoglobin) of various sea animals (like the cuttlefish), where the blood is blue in the arteries and colorless in the veins. It also occurs in the red coloring matter of the feathers of certain birds. (Church.)

Preparation.—*From copper pyrites* (Cu_2S,Fe_2S_3) (Copper smelting). The ore is sorted, that is, those pieces rich in copper are picked out and broken up, whilst the part less rich in metal is powdered and sifted.

(1.) *Calcination of ore.*—The ore is first *calcined or roasted*, whereby the arsenic and part of the sulphur are volatilized as As_2O_3 and SO_2, cuprous sulphide with some oxide, and ferric oxide (converted from ferric sulphide) together with some sulphide, remaining. The ferric sulphide is far more easily oxidised than the cuprous sulphide. Hence the chief part of the Cu_2S remains unaltered.

[The fumes given off during roasting are called "*copper smoke*," and contain As, As_2O_3, SO_3, SO_2, and HF, the latter being derived from the fluor spar contained in the ore.]

(2.) *Fusion for coarse metal.*—The calcined ore is now mixed with sand and a slag containing a quantity of silicate, fluor spar being added if necessary, to increase the fluidity of the slag. The mixture is now intensely heated in the "ore furnace." The following changes occur :—The cuprous oxide acts on the ferric sulphide present, cuprous sulphide and ferric oxide being formed. But inasmuch as there is more ferric sulphide in the ore than can be oxidized by the cuprous oxide present, the excess of the fused ferric sulphide, together with the cuprous sulphide, sink to the bottom of the furnace to form what is called the "*mat*" or "*coarse metal*" ($=CuFeS_2$). This coarse metal is granulated by being run into water whilst liquid.

The ferric oxide present combines with the silica to form a fusible slag (silicate of iron) ($FeSiO_3$), which is used for building purposes.

(3.) *Calcination of the coarse metal.*—The coarse metal is now calcined, whereby any sulphide of iron present is converted into oxide.

(4.) *Fusion for white metal.*—The roasted coarse metal is now fused with silica, and with an ore rich in cupric oxide, whereby any unchanged iron sulphide is converted into oxide. The whole of the iron which is now present as ferric oxide combines with the silica to form a fusible slag, the "mat," or "regulus of white metal," or the "*fine metal*," as it is now called, being nearly pure cuprous sulphide (Cu_2S).

Sometimes the roasting is carried further, so that a portion of the sulphide becomes reduced. This reduced portion sinks to the bottom, along with most of the foreign metals present, these parting with their sulphur more readily than the copper. Hence the *upper* part of the ingot is always the purest, and is known as "*best selected copper*," whilst the *under* portion, containing the impurities, is known as "*tile copper*."

(5.) *Roasting for blistered copper.*—The fine metal (Cu_2S) is now roasted, whereby some of the copper becomes converted into CuO, the sulphur escaping as SO_2. Hence the mass after roasting consists of Cu_2S and CuO. The temperature is now raised, when mutual decomposition occurs between the cuprous sulphide and the cupric oxide metallic copper and sulphurous anhydride (which escapes) being formed ($Cu_2S + 2CuO = SO_2 + 4Cu$). This copper is called "*pimple*," or "*blistered copper*," blisters being formed upon the surface of the metal by the escape of the last portions of SO_2.

(6.) *Refining.*—This is effected by melting the copper, so as to oxidize the last traces of sulphur and of foreign metals present, such as Fe, Sn, Pb, etc. Some cuprous oxide (Cu_2O) is produced during the process, a part of which forms a slag with any sand present, another part being dissolved by the metallic copper. The presence of this cuprous oxide in copper renders the metal brittle ("*dry copper*").

(7.) *Toughening* (*poling*).—After the removal of the slag, some anthracite is thrown on the surface of the melted metal, to prevent further oxidation. It is then well stirred with a pole of young wood (*poled*), the combustible gases given off by the wood burning at the expense of any oxide present in the liquid metal. The presence of a little suboxide in the metal is said to render it tough. Hence, both "over-poling" (that is, where the whole of the cuprous oxide is decomposed), and "under-poling" (that is, where too much is left), are to be avoided. When the copper is properly poled, it is known as "tough cake."

In the preparation of copper from the oxide, or from the carbonate, all that is necessary is to reduce a mixture of the copper salt with carbon and silica, in a wind furnace.

Wet process.—The burnt pyrites, after heating to separate the sulphur, often contains 4 per cent. of copper. By roasting this residue with 20 per cent. of common salt, the copper, as cupric chloride, may be extracted with water, and the metal precipitated from the solution by means of scrap iron.

Impurities.—Sulphur (which injures the malleability of the copper), arsenic, phosphorus (which increases its hardness), tin, antimony, nickel, bismuth, silver, and selenium, are the ordinary impurities of commercial copper.

A pure copper may be obtained by the electrolysis of a solution of cupric sulphate, or by heating the oxide in a current of hydrogen.

Properties.—(*a.*) *Physical.* A red metal (copper color), having a metallic taste and a peculiar smell. A very fine copper leaf transmits a greenish blue light. The metal occurs, and may be prepared artificially, in cubes and octahedra. It is a very heavy (Sp. gr. 8·9), hard, ductile, malleable, and sonorous metal. It fuses at 1996° F. (1091° C.). In a molten condition, it absorbs various gases (such as CO), which escape as the metal solidifies, a property that unfits it for fine castings. The finely-divided metal absorbs 0·6 its volume of hydrogen. At a white heat it is said to be slightly volatile. It is a good conductor both of heat and electricity.

(*β.*) *Chemical.*—Copper is not affected by dry air at ordinary temperatures, but in moist air (or in contact with water) it becomes coated with a basic carbonate. In air at a red heat, it oxidises rapidly, black scales of cupric oxide (CuO) pealing off from the surface of the metal. When finely divided, it burns like tinder. The metal burns in the oxyhydrogen blowpipe, coloring the flame green. It is not acted upon by pure water, nor indeed has a current of steam any action on the red-hot metal. When placed in solutions of chlorides, as in *sea-water*, the metal becomes coated with the green *oxychloride* ($CuCl_2,3CuO,4H_2O$). Copper vessels are, therefore, dangerous for culinary purposes, inasmuch as a certain quantity of the metal is dissolved when solutions of common salt or of acids (such as vinegar, rhubarb, etc.), or of liquids containing fatty and oily matter, are boiled in contact with the metal.

It is not soluble in dilute HCl or H_2SO_4 if air be excluded, but in the presence of air, or in contact with an element more electro-negative than itself (such as Pt), it rapidly dissolves in the dilute acids. Concentrated sulphuric acid has no action upon it, but nitric acid and boiling sulphuric acid dissolve it. With the former, nitric oxide (NO) is evolved, and with the latter, sulphurous anhydride (SO_2). Liquid hydrochloric acid acts upon the finely-divided metal. evolving hydrogen. Dilute nitric acid acts on it energetically, even in the cold. When a current of hydrochloric acid gas is passed over the red-hot metal, hydrogen is set free, and cuprous chloride (Cu_2Cl_2) formed. Ammonia dissolves copper (*cupr-ammonia*), forming a deep blue solution, but the fixed alkalies have very little action upon it. The metal is precipitated from its solutions by readily oxidizable bodies such as iron, zinc, phosphorus, etc. It combines with chlorine energetically, thin leaves of metallic copper catching fire so soon as they are exposed to the action of the gas.

Uses.—It is largely used for electrical purposes, its conductivity being greater than that of any other known metal excepting silver. It is also used for electrotyping ; for coinage ; for alloys, etc. The composition of certain alloys is stated in the following table (from Bloxam). The alloys of copper are harder than the metal itself.

	Copper.	Zinc.	Tin.	Iron.	Nickel.	Aluminium
Brass	64·0	36·0				
Muntz Metal	60 to 70	40 to 30				
German silver	51·0	30·5	—	—	18·5	
Aich (or Gedge's) metal	60·0	38·2	—	1·8		
Bell metal	78·0	—	22·0			
Speculum metal	66·6	—	33·4			
Bronze metal	80·0	4·0	16·0			
Gun metal	90·5	—	9·5			
Bronze coinage	95·0	1·0	4·0			
Aluminium bronze ..	90·0	—	—	—	—	10·0

Compounds of Copper ($Cu = 63·5$).

		COMPOUNDS.	Formulæ (General).	Molecular Weight Anhydrous Salts.	Specific Gravity.	Cu per Cent.
1		Cuprous hydride	Cu_2H_2	129·0		98·44
2		,, quadrantoxide	Cu_4O	270·0		
3	Oxides.	,, oxide (red oxide)	Cu_2O	143·0	3·85	88·79
4		,, hydrate	$4Cu_2O,H_2O$			
5		Cupric oxide (black oxide)	CuO	79·5	6·5	79·85
6		,, hydrate	CuH_2O_2			
7	Chlorides.	Cuprous chloride	Cu_2Cl_2	198·0	3·37	64·10
8		Cupric chloride	$CuCl_2,2H_2O$	134·5+36	3·05	47·17
9		Hydrated cupric oxychloride of copper	$CuCl_2,3CuH_2O_2$			
		[Corresponding bromides and iodides have been prepared.]				
10		Cuprous nitride	Cu_6N_2	408·4		93·14
11	Sulphides.	,, sulphide (copper glance)	Cu_2S	159·0	5·5	79·84
12		Cupric sulphide	CuS	95·5	3·8	66·45
13		,, pentasulphide	CuS_5			
14		Cuprous phosphide	Cu_6P_2			
15		Cupric ,,	Cu_3P_2	252·2		75·41
16		,, selenide	$CuSe$			
17		Cuprous arsenide	Cu_6As_2			
18		Cupric sulphate (blue vitriol)	$CuSO_4,5H_2O$	159·5+90	2·25	31·84
19		,, nitrate	$Cu2NO_3,3H_2O$	187·5+54		33·83
20		Hydrated oxy-carbonate of copper (azurite)	$2CuCO_3,CuH_2O_2$	344·2	3·8	55·22
21		Hydrated dibasic carbonate (malachite)	$CuCO_3,CuH_2O_2$	220·8	3·9	57·42
22		Dicupric carbonate (mysorin)	$2CuO,CO_2$	202·8		62·52
23		Cupric phosphate (normal)	$Cu_3P_2O_83H_2O$ $CuHPO_4$			
24		,, arsenate	$Cu_3As_2O_82H_2O$			
25		,, arsenite	$CuHAsO_3$	187·5		
26		,, silicates	$CuOSiO_2H_2O$ $CuOSiO_22H_2O$			

COMPOUND OF COPPER AND HYDROGEN.

Cuprous hydride ... ... Cu_2H_2.

(1.) Cuprous Hydride (Cu_2H_2). *Molecular Weight,* 129.

Preparation.—By heating a cupric sulphate solution with hypophosphorous acid to 140° F. (60° C.). (See page 159.)

Properties.—A black powder, evolving hydrogen when heated. It catches fire when exposed to the action of chlorine. Hydrochloric acid forms with it cuprous chloride, the combination being accompanied by the evolution of hydrogen ($Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2$).

COMPOUNDS OF COPPER AND OXYGEN.

Cuprous quadrantoxide ... ... Cu_4O.
Cuprous oxide (red oxide) ... ... Cu_2O.
Cupric oxide (black oxide)... ... ... CuO.

(2.) **Cuprous Quadrantoxide** (Cu_4O). This oxide is only known as a green hydrate, and may be prepared by digesting a cupric salt in closed vessels with an excess of stannous chloride dissolved in a large excess of potassic hydrate. It is a very unstable compound, and possesses great affinity for oxygen.

(3.) **Cuprous Oxide,** *Suboxide* or *Red oxide of copper* (Cu_2O). *Molecular weight* =143·0. *Specific gravity,* 5·5.

Natural History.—Found native as red copper ore, in octahedral crystals, having a specific gravity varying from 3·8 to 6.

Preparation.—(1.) By boiling grape sugar in a solution of cupric sulphate, in the presence of an excess of potassium hydrate.

(2.) By igniting a mixture of 5 parts of cupric oxide (CuO) and 4 parts of copper filings.

(3.) By boiling a mixed solution of cupric sulphate, sodium sulphite, and sodium carbonate ($2CuSO_4 + 2Na_2CO_3 + Na_2SO_3 = Cu_2O + 3Na_2SO_4 + 2CO_2$).

(4.) By acting on an ammoniacal solution of cupric oxide with metallic copper, air being excluded. By this means the *blue* solution of CuO becomes a *colorless* solution of Cu_2O ($Cu + CuO = Cu_2O$).

[(5.) Preparation of *Cuprous hydrate* ($4Cu_2O,H_2O$). By decomposing cuprous chloride with potassic hydrate.]

Properties.—(*a.*) *Physical.* A reddish-yellow powder. Fuses at a red heat, if air be excluded. Insoluble in water.

(*β.*) *Chemical.* In the moist state, cuprous oxide is slowly oxidized by air. It is a feeble base. There are no cuprous oxy-salts (except sulphites and certain double sulphites), the oxy-acids decomposing cuprous oxide, forming with it a mixture of a cupric salt and metallic copper. Nitric acid converts cuprous oxide into cupric nitrate with evolution of nitric oxide; whilst sulphuric acid (hot) converts it into cupric sulphate, with evolution of sulphurous acid. Hydrochloric acid converts it into cuprous chloride (Cu_2Cl_2). It is soluble in ammonia, *the solution being colorless*, but in the presence of a mere trace of oxygen the solution turns blue from the formation of cupric oxide.

It is slightly soluble in metallic copper, which it renders what is called "dry" or "brittle."

Use.—For stained glass, to which it imparts a fine *red* color.

(5.) **Cupric Oxide**; *Copper monoxide; Black oxide of copper* (CuO). *Molecular weight*, 79·4. *Specific Gravity*, 6·5.

Preparation.—(1.) By heating the metal in air.

(2.) By the ignition of cupric nitrate or carbonate ($2Cu2NO_3 = 2CuO + 2N_2O_4 + O_2$).

(3.) As *cupric hydrate* (CuH_2O_2). By adding potassic hydrate in excess to a solution of a cupric salt. The hydrate (blue) becomes anhydrous (black) by boiling in water.

Properties.—(*a.*) *Physical.* Cupric oxide fuses at a white heat, becoming an oxide said to have the formula Cu_5O_3 (?). The hydrate (CuH_2O_2) has a light blue color, but the anhydrous oxide is black. Although a hygroscopic body, absorbing water freely from the air, it is insoluble in water, but is soluble in oils and fats. Hence the danger of copper for culinary purposes.

(*β.*) *Chemical.* It is soluble in most acids, forming cupric salts that are isomorphous with magnesium salts. It combines when fused with the fixed alkalies. The hydrate is soluble in ammonia water, forming a blue solution (cupr-ammonia), having the property of dissolving cellulose, which cellulose is reprecipitated from solution by an acid. The blue solution is also formed when copper filings are shaken up in an ammonia solution in the presence of air, a portion of the ammonia becoming oxidised simultaneously with the copper, white fumes of ammonic nitrite being formed.

When heated to redness with carbon or in a current either of hydrogen or of carbonic oxide, the metal is reduced.

Uses.—In organic combustion analysis to furnish oxygen to the organic body. It is used to stain glass a fine *green* color.

COMPOUNDS OF COPPER AND CHLORINE.

Cuprous chloride	Cu_2Cl_2.
Cupric chloride	$CuCl_2$.

(7.) Cuprous Chloride.—*Subchloride of copper* (Cu_2Cl_2). *Molecular weight* = 197·4. *Specific gravity,* 3·3.

Preparation.—(1.) By the action of hydrochloric acid on copper in the presence of air ($2Cu_2 + 4HCl + O_2 = 2Cu_2Cl_2 + 2H_2O$).

(2.) By distilling one part of copper filings with two parts of mercuric chloride.

(3.) By boiling together cupric chloride and sugar.

(4.) By heating dry cupric chloride in a current of dry ammonia.

(5.) By boiling a solution of cupric chloride in HCl with copper filings, to which a few drops of a solution of platinum chloride is added.

(6.) By the action of stannous chloride on a cupric salt ($2CuCl_2 + SnCl_2 = Cu_2Cl_2 + SnCl_4$).

Properties.—(*a.*) *Physical.* A white compound, turning violet when moistened and exposed to light. It may be obtained in tetrahedral crystals from its solution in hot hydrochloric acid. It fuses to a yellow mass, and at a high temperature is volatile. It is insoluble in water.

(*β.*) *Chemical.* Hydrochloric acid dissolves it. The colorless solution thus formed throws down cuprous chloride on the addition of water. The acid solution readily absorbs carbonic oxide, from which solution, the unstable crystalline compound ($Cu_2Cl_2,CO,2H_2O$) may be obtained. It also absorbs oxygen, when the solution becomes brown and deposits a green cupric oxychloride ($CuCl_2,3CuO,4H_2O$), known as "*Brunswick green.*" This latter substance is also found native (*atacamite*).

Ammonia solution dissolves it, forming (air being excluded) a colorless liquid. This solution rapidly absorbs oxygen, becoming of a deep blue color. Cuprous chloride gives a red precipitate with acetylene, for which it constitutes a delicate test. With argentic nitrate it deposits silver, the ammonia holding the silver chloride and copper nitrate in solution ($Cu_2Cl_2 + 4AgNO_3 = 2(Cu2NO_3) + 2AgCl + Ag_2$).

Cuprous chloride is soluble in sodium thiosulphate, the solution possessing the power of absorbing various gases of the acetylene series. It is also soluble in potassic chloride, forming with it the double salt $4KCl,Cu_2Cl_2$. It is also soluble in ammonic chloride, white dodecahedral crystals of $Cu_2Cl_2\,(NH_3)_2$ being deposited from the fresh solution, or blue cubical crystals of $Cu''Cl_2(NH_3)_2,2NH_4Cl$ after its prolonged exposure to air.

(8.) Cupric Chloride.—*Chloride of copper* ($CuCl_2$).

Preparation.—(1.) By dissolving copper in aqua regia, or by dissolving cupric oxide or carbonate in hydrochloric acid and crystallizing ($=CuCl_2,2H_2O$).

(2.) By the spontaneous combustion of copper in chlorine.

Properties.—Green deliquescent crystals (specific gravity, 2·5), becoming blue when dried. The solution of the chloride in alcohol burns with a green flame. The salt fuses, and is decomposed at a red heat into chlorine and cuprous chloride. It is very soluble both in alcohol and in water, the aqueous solution appearing green when concentrated and blue when dilute. It forms double salts with the alkaline chlorides (*e.g.*, $CuCl_2,2KCl,2H_2O$). The anhydrous chloride absorbs ammonia, becoming a blue powder ($CuCl_2,6NH_3$). Cuprammonic chloride, having the formula ($CuCl_2,2NH_3$), is formed when the powder is heated to 202° F. (150° C.). Oxy-chlorides are formed by digesting together the chlorate and hydrate.

Cuprous Iodide (Cu_2I_2). A white crystalline powder. Fuses at a red heat. (A cupric iodide is not known.)

Preparation.—By precipitating a solution of cupric sulphate with potassium iodide ($2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2$).

Cuprous Bromide or *subbromide of copper* (Cu_2Br_2) and **Cupric Bromide** ($CuBr_2$) have been prepared.

(10.) Tricupric Nitride (Cu_6N_2).

Preparation.—By passing ammonia gas over cupric oxide heated to 482° F. (250° C.).

The nitride is a dark green powder.

COMPOUNDS OF COPPER AND SULPHUR.

Cuprous sulphide	Cu_2S.
Cupric sulphide	CuS.
Cupric pentasulphide	CuS_5.

(11.) **Cuprous Sulphide.**—*Subsulphide of copper* (the "fine metal" of the copper smelter) (Cu_2S). This body is found native in six-sided prisms, as "copper glance" or "Redruthite." *Copper pyrites* is a cuprous-ferric-sulphide (Cu_2S,Fe_2S_3).

Preparation.—By melting together three parts of sulphur and eight of copper.

Properties.—Fusible by heat (Sp. gr. 5·5). Soluble (with decomposition) in nitric acid and in aqua regia, but insoluble in hydrochloric acid.

(12.) **Cupric Sulphide.**—*Sulphide of copper* (CuS). Found native as "indigo copper," "blue copper" or "covellin."

Preparation.—(1.) By heating finely-divided copper with sulphur, the heat being kept below the melting-point of the sulphur. (2.) (As *a hydrate.*) By precipitating cupric salts with sulphuretted hydrogen.

Properties.— Sp. gr. 4·6. By heat the cupric sulphide becomes cuprous sulphide, if air be excluded. The hydrated cupric sulphide, by exposure to air, rapidly becomes sulphate. Cupric sulphide is soluble in nitric acid ; insoluble in sodium or potassium sulphides ; somewhat soluble in yellow ammonic sulphide ; very soluble in potassic cyanide. By washing the precipitated sulphide with sulphuretted hydrogen water, the precipitate finally dissolves, yielding a brown liquid, supposed to contain a colloidal modification of the sulphide.

(13.) **Cupric Pentasulphide** (CuS_5).

Preparation.—By decomposing a cupric salt with an alkaline pentasulphide.

Properties.—A black precipitate, insoluble in potassic carbonate.

(14.) **Cupric Phosphide.**—*Phosphide of copper* (Cu_2P_2).

Preparation.—By boiling phosphorus in a cupric sulphate solution.

Properties.—A black substance, decomposed by heat ($3Cu_2P_2 = Cu_6P_2 + 2P_2$). Phosphoretted hydrogen is evolved when the phosphide is added to a solution of potassic cyanide.

CUPRIC OXYSALTS.

(16.) **Cupric Sulphate.**—*Sulphate of copper; blue vitriol; blue stone; blue copperas* ($CuSO_4,5H_2O$).

Molecular weight, 159·4+90. *Specific gravity, crystals,* 2·25 ; *anhydrous,* 3·63.

Preparation.—(1.) By dissolving the metal or its oxide in sulphuric acid.

(2.) By oxidising the sulphide. Copper pyrites is first roasted, and the resulting mass treated with water. By this means most of the iron remains behind as oxide. The iron in the copper sulphate is got rid of by successive crystallizations, nitric acid being added to convert the ferrous sulphate into a ferric salt, ferric sulphate differing from ferrous sulphate in not crystallising with cupric sulphate.

(3.) As a secondary product in refining silver (*vide* Silver); a cupric sulphate being formed from the copper plates used to throw down the silver from its solution as a sulphate.

Properties.—It is found in the form of transparent, blue, efflorescent, doubly oblique crystals ($CuSO_4,5H_2O$). When these are heated to 212° F. (100° C.) they become $CuSO_4,H_2O$, and at 392° F. (200° C.) the salt changes to a white anhydrous powder ($CuSO_4$). (This last H_2O molecule is regarded as water of constitution, the rest as water of crystallisation.) The anhydrous white salt combines energetically with water, the blue salt being re-formed and great heat thereby evolved. At a very high temperature $CuSO_4$ is converted into cupric oxide, oxygen and sulphurous anhydride being evolved.

The crystals are insoluble in alcohol, but soluble in water (1 in 4 at 60° F., 1 in 2 at 212° F.). The solution is acid.

Potassic hydrate, added to a solution of the salt, throws down a blue hydrated cupric oxide or "blue verditer" (CuH_2O_2). The powdered crystals of the sulphate rapidly absorb hydrochloric acid gas, with evolution of heat. The anhydrous salt rapidly absorbs ammonia gas, forming $CuSO_4,5NH_3$ (Rose). Cupric sulphate forms double salts with the sulphates of ammonium and potassium, isomorphous with the corresponding zinc and magnesium salts ($CuSO_4,K_2SO_4,6H_2O$).

Several basic cupric sulphates are known: of these may be mentioned a *tribasic sulphate*, $CuSO_4,2CuH_2O_2$, and *brochantite*, $CuSO_4,3CuH_2O_2$.

The *ammonio-sulphate of copper* ($CuSO_4,4NH_3,H_2O$) is formed when a solution of cupric sulphate, containing an excess of ammonia, is carefully evaporated to dryness. On heating this ammonio-sulphate to 352° F. (150° C.) a green powder is formed ($CuSO_42NH_3$).

(17.) Cupric Nitrate ($Cu2NO_3,3H_2O$).

Preparation.—By dissolving copper or cupric oxide in nitric acid.

Properties.—A blue crystalline deliquescent salt, soluble in alcohol, decomposed by *slight* heat into an insoluble basic nitrate ($Cu2NO_3, 3CuH_2O_2$), and by an *intense* heat into the black oxide (CuO). It is an active oxidizing body. It is used in dyeing and calico printing, where an oxidizing agent may be required.

Cupric Arsenate ($Cu_3As_2O_8$) is prepared by heating calcium arsenate with cupric nitrate. It is a blue powder.

Cupric Arsenite or *Scheele's green* ($CuHAsO_3$) is a green powder, prepared by the action of an alkaline arsenite on a cupric salt. It is insoluble in water, but soluble in caustic potash, yielding a blue liquid. A mixture of cupric arsenite and acetate ($3CuAs_2O_4,Cu2C_2H_3O_2$) constitutes "Schweinfurt green."

The **Cupric Carbonates** known, are *a hydrated oxycarbonate* or "chessylite" ($2CuCO_3,CuH_2O_2$; Sp. gr. 3·8), and *a hydrated dibasic carbonate* or "malachite" ($CuCO_3,CuH_2O_2$; Sp. gr. 3·7). *Verdigris*, the compound formed by the action of air and water jointly on copper, has much the same composition. "Mineral green," moreover, has also the same composition as this latter compound, and is prepared by acting on a solution of cupric sulphate with sodium carbonate. If the precipitate be boiled in the solution, CuO is formed.

Cupric Phosphates.—If cupric carbonate be digested with dilute phosphoric acid and warmed, the compound $Cu_3P_2O_8,3H_2O$ is formed. The compound $CuHPO_4$ results when a copper salt is added to an excess of an alkaline phosphate. Basic phosphates have been prepared, and occur naturally as *tagilite* and *libethinite*.

REACTIONS OF COPPER COMPOUNDS.

Flame; colored blue or green.

Spectrum spark gives a series of lines, those in the green being very prominent.

A.—CUPROUS COMPOUNDS :—

Caustic alkalies.—Yellow ppt. of cuprous hydrate ($4Cu_2O,H_2O$), becoming red (Cu_2O) on boiling.

B.—CUPRIC COMPOUNDS :—

Caustic alkalies.—A blue ppt. (CuH_2O_2), becoming black on boiling.

[CuH_2O_2 is soluble in excess of alkalies, if sugar, tartaric acid, etc., be present.]

Ammonia.—A blue ppt. (CuH_2O_2), soluble in excess, forming a deep blue liquid.

Sulphuretted hydrogen gives in acid solution a black ppt. of CuS, soluble in potassic cyanide.

Potassic ferrocyanide.—A brown ppt. insoluble in HCl.

The metal may be precipitated from all solutions by zinc and iron.

Blowpipe.—Metal reduced when copper compounds are heated on charcoal with sodic carbonate.

Borax-bead.—In the *oxidizing flame* the bead is green when hot, and blue when cold. In the *reducing flame* the bead is red from the presence of reduced copper.

BISMUTH ($Bi''' = 208{\cdot}2$).

Specific gravity, 9·83. *Fuses at* 507·2° F. (264° C.). *Atomicity, triad* ($Bi'''Cl_3$) ; *and pentad* ($Bi^v_2O_5$). *Specific heat,* 0·0308.

Natural History.—Bismuth is commonly found in a free state, but it also occurs as an *oxide* in "bismuth ochre" (Bi_2O_3), and as a *sulphide* in "bismuth glance" (Bi_2S_3) and *bismuthite* (Bi_2S_5). These minerals are rare.

Certain sulpho-bismuthites have been found in nature, such as kobellite (Bi_2PbS_6). A telluride of bismuth (Bi_2Te_3) is also known.

Preparation.—(1.) By simple fusion of the ore in inclined iron cylinders, the metal flowing away and leaving the matrix in the tube. Thus prepared, bismuth usually contains certain impurities, such as arsenic, sulphur, and silver, the latter being frequently extracted by cupellation.

(2.) By reduction of the roasted ore by heating with carbon.

Properties.—(*a.*) *Physical.* A hard, brittle, reddish-white metal, crystallizing in large cubes. Specific gravity, 9·83. It is slightly volatile at high temperatures. It fuses at 507° F. (264° C.), expanding at the moment of solidification. By its admixture with other metals, the fusing point of the alloy is often lowered to a remarkable extent.

(*β.*) *Chemical.* Bismuth is only slightly affected by air at ordinary temperatures, but it oxidizes rapidly (forming Bi_2O_3) at a red heat. Nitric acid dissolves it freely ; boiling sulphuric acid oxidizes it, SO_2 being evolved ; hydrochloric acid and dilute sulphuric acid have no action upon it. It combines rapidly with chlorine, bromine, iodine, and sulphur.

No compound of bismuth with hydrogen is known.

Uses.—It occurs as a bye-product in the manufacture of smalt. It is used for alloys. Its use in type metal depends on the property it possesses of expanding as it solidifies, whereby the sharpness of the impression is increased.

"*Fusible metal*" or "*Rose's metal,*" is a mixture of two parts of bismuth with one of tin and one of lead, and melts at 201° F. (94° C.). By letting a plate of the fusible alloy into a boiler, the metal fuses and allows vent to the steam so soon as the temperature of the steam reaches the melting-point of the alloy. By this means boiler explosions are prevented.

Its use in solder depends on its power of lowering the fusing point of the metals with which it is associated.

Compounds of Bismuth (Bi = 210).

	COMPOUNDS.	Formulæ (General).	Molecular Weight.	Specific Gravity.	Bi per cent.
1	Bismuthous oxide	BiO	226		92·85
2	Bismuthic oxide	Bi_2O_3	468·0	8·211	89·74
	Bismuthic hydrate	Bi_2O_3, H_2O	486		
3	Metabismuthous acid	$HBiO_2$	243·0		
4	Bismuthous bismuthate	(Bi_2O_3,Bi_2O_5) or Bi_2O_4			
5	Bismuthic anhydride	Bi_2O_5	500		83·87
6	Metabismuthic acid	$HBiO_3$	259·0		
7	Bismuthous chloride	$BiCl_3$	316·5	4·56	66·13
8	,, oxychloride	$BiClO$	261·5		80·15
9	Dibismuthous tetrachloride	Bi_2Cl_4	562·0		74·55
10	Bismuthous bromide	$BiBr_3$	450		46·42
11	,, oxybromide	$BiBrO$			68·42
12	Bismuthous iodide	BiI_3	591		35·31
13	,, oxyiodide	$BiIO$			59·25
14	,, fluoride	BiF_3	267·0		78·49
15	Bismuthous sulphide	BiS	242·0		86·66
16	Bismuthic sulphide	Bi_2S_3	516·0		81·25
17	,, nitrate	$Bi3NO_3,5H_2O$	394·0	2·376	52·79
18	,, sulphate	Bi_23SO_4			

COMPOUNDS OF BISMUTH WITH OXYGEN, ETC.

1. Bismuthous oxide ... ... BiO.
2. { Bismuthic oxide ... ... Bi_2O_3.
   Bismuthic hydrate ... ... Bi_2O_3,H_2O.
3. Metabismuthous acid ... ... $(Bi_2O_3,H_2O) = HBiO_2$.
4. Bismuthous bismuthate ... (Bi_2O_3,Bi_2O_5) or Bi_2O_4.
5. Bismuthic anhydride ... ... Bi_2O_5.
6. Metabismuthic acid ... ... $(Bi_2O_5,H_2O) = HBiO_3$.

(1.) **Bismuthous Oxide** (BiO). *Preparation.*—By reducing bismuthous chloride with stannous chloride in the presence of an excess of potash.

Properties.—Oxidizes spontaneously. Burns freely in air or in oxygen, forming Bi_2O_3.

(2.) **Bismuthic Oxide**; *Sesquioxide* or *Trioxide of Bismuth* (Bi_2O_3). *Specific gravity*, 8·2.

It is found native as "bismuth-ochre."

Preparation.—(1.) By heating bismuth in air. (2.) By igniting the nitrate, carbonate or hydrate.

Properties.—A yellow, easily fusible powder (Sp. gr. 8·2), soluble in HCl, in HNO_3, and in H_2SO_4, forming *bismuthous chloride* ($BiCl_3$), *bismuthous nitrate* ($Bi3(NO_3)$), and *bismuthous sulphate* ($Bi_23(SO_4)$), respectively. Ammonia precipitates the oxide as a hydrate from a solution of a salt of bismuth (Bi_2O_3,H_2O). (*See* Metabismuthous Acid.)

(3.) **Metabismuthous Acid** ($Bi_2O_3,H_2O = HBiO_2$); ***Bismuthic hydrate.***

Preparation.—By adding ammonia to a solution of bismuthous nitrate in dilute nitric acid, and drying at 212° F. (100° C.) When heated, a residue of Bi_2O_3 remains. By the fusion of Bi_2O_3 with sodium carbonate, a *sodium metabismuthite* ($NaBiO_2$) is formed.

(5.) **Bismuthic Anhydride** (Bi_2O_5).

Preparation.—(*a.*) When bismuthic oxide suspended in a solution of potassic hydrate is treated with chlorine, *metabismuthic acid* ($HBiO_3$) is formed :—

$4KHO$	$+$	$2Cl_2$	$+$	Bi_2O_3	$=$	$2HBiO_3$	$+$	$4KCl$	$+$	H_2O.
Potassic hydrate	+	Chlorine	+	Bismuthic oxide	=	Metabismuthic acid	+	Potassic chloride	+	Water.

(*β.*) By heating the acid so formed ($= Bi_2O_5,H_2O$) to 269° F. (132° C.), water is expelled and *bismuthic anhydride* (Bi_2O_5) remains.

Properties.—A red powder, decomposed by heat ($2Bi_2O_5 = Bi_2O_3, Bi_2O_5$ (or $2Bi_2O_4$) $+ O_2$) into *bismuthous bismuthate.* When bismuthic anhydride is heated in a current of hydrogen, Bi_2O_3 is formed. Heated with hydrochloric acid it forms bismuthous chloride, chlorine being evolved ($Bi_2O_5 + 10HCl = 2BiCl_3 + 5H_2O + 2Cl_2$). When treated with nitric, sulphuric or sulphurous acids, a bismuthous nitrate or sulphate is formed accordingly, oxygen being liberated in the case of the nitric and sulphuric acids ($Bi_2O_5 + 6HNO_3 = 2Bi3NO_3 + 3H_2O + O_2$).

(6.) **Metabismuthic Acid** ($Bi_2O_5,H_2O = HBiO_3$); ***Bismuthic hydrate.***

Preparation.—(*Vide* (*a*), under Bismuthic Anhydride.) The compounds of this acid are very unstable.

Compounds of Bismuth with Chlorine, etc.

7.	Bismuthous chloride	$BiCl_3$.
8.	Bismuthous oxychloride	$BiClO$.
9.	Dibismuthous tetrachloride	Bi_2Cl_4.
10.	Bismuthous bromide	$BiBr_3$.
11.	Bismuthous oxybromide	$BiBrO$.
12.	Bismuthous iodide	BiI_3.
13.	Bismuthous oxyiodide	$BiIO$.
14.	Bismuthous fluoride	BiF_3.

(7, 8, 9.)—**Bismuthous Chloride.**—*Trichloride of Bismuth* ($BiCl_3$).

Preparation.—(1.) By heating bismuth in a current of dry chlorine ($Bi_2 + 3Cl_2 = 2BiCl_3$).

(2.) By distilling a mixture of bismuth and mercuric chloride ($Bi_2+6HgCl_2 = 2BiCl_3+3Hg_2Cl_2$).

(3.) By distilling a solution of bismuth in nitro-hydrochloric acid.

Properties.—A fusible, volatile, deliquescent solid. Specific gravity of solid, 4·56; of vapor, 11·16. It is soluble in dilute hydrochloric acid, but is decomposed by admixture with pure water into bismuthous oxychloride ("pearl white") and hydrochloric acid ($BiCl_3+H_2O = BiClO+2HCl$). Bismuthous oxychloride is insoluble both in tartaric acid and in ammonic sulphide.

By heating bismuthous chloride with metallic bismuth, *dibismuthous tetrachloride* (Bi_2Cl_4) is formed.

COMPOUNDS OF BISMUTH AND SULPHUR.

15.	Bismuthous sulphide	BiS.
16.	Bismuthic sulphide	Bi_2S_3.

(15.) Bismuthous Sulphide (BiS or Bi_2S_2) is found native, and may be prepared artificially by fusing together sulphur and bismuth.

(16.) Bismuthic Sulphide (Bi_2S_3) is found native as "bismuth glance."

Preparation.—(1.) By fusing together sulphur and bismuth in proper proportions.

(2.) By passing sulphuretted hydrogen through a solution of a bismuth compound ($2BiCl_3+3H_2S = Bi_2S_3+6HCl$).

Properties.—A fusible, dark grey, heavy substance (Sp. gr. 6·4). It is soluble in nitric acid, but is insoluble in dilute sulphuric or in hydrochloric acid, as well as in the alkaline hydrates or sulphhydrates.

OXYSALTS OF BISMUTH.

(17.) Bismuthous Nitrate ($Bi3NO_3,5H_2O$). Sp. Gr. 2·3.

Preparation.—By dissolving the metal in nitric acid.

Properties.—When the acid solution is acted on with a quantity of water, a precipitate is thrown down of a *basic nitrate*, known in pharmacy as *subnitrate*, or *trisnitrate of bismuth* (flake white; magistery of bismuth) ($Bi3NO_3,Bi_2O_3,3H_2O$). This compound is employed in medicine as a sedative.

REACTIONS OF BISMUTH COMPOUNDS.

(1.) *Sulphuretted hydrogen.*—A brown ppt. of Bi_2S_3 in acid solutions; precipitate insoluble in ammonium sulphide.

(2.) *Ammonia and caustic alkalies.*—A white ppt., insoluble in excess, unless tartaric or citric acid be present, when the precipitate redissolves on the addition of an excess of the reagent.

(3.) *Blowpipe* (reducing flame) *on charcoal.*—A brittle metallic bead, surrounded by a yellow incrustation of oxide.

CADMIUM ($Cd'' = 112$).

Atomic and molecular weight, 112 (p. 39). *Specific gravity*, 8·604. *Fuses at* 442° F. (228° C.). *Specific heat*, 0·056. *Boils at* 1580° F. (860° C.). *Atomicity, dyad* ($CdCl_2$; CdO).

History.—Discovered by Stromeyer and Hermann simultaneously (1818).

Natural History.—Found in many zinc ores. Occurs also as a sulphide (Greenockite).

Preparation.—When zinc ore is distilled, the cadmium (a constant accompaniment of zinc) passes over in the first distillate, owing to its greater volatility, its presence in the zinc being indicated by a *brown* flame (brown blaze) produced when the primary products are fired. The distillate thus obtained (a mixture of cadmium and zinc) is dissolved in dilute sulphuric acid, and H_2S passed through the solution. The yellow precipitate of CdS formed (the zinc remaining in solution) is then dissolved in hydrochloric acid, to which an excess of ammonium carbonate is added. The precipitated carbonate of cadmium ($CdCO_3$) (copper and arsenic remaining in solution), becomes on ignition cadmium oxide (CdO), from which the metal may be obtained by distillation with carbon.

Properties.—(*a.*) *Physical.* A white, soft, crystalline metal, marking paper like lead, and crackling like tin when bent. Sp. gr. 8·6. At common temperatures it is both malleable and ductile, but when heated to 176° F. (80° C.) it becomes brittle. It fuses at 442° F. (228° C.), and boils at 1580° F. (860° C.). The cadmium atom appears to occupy in the state of vapor twice the space of the hydrogen atom (p. 39).

(*β.*) *Chemical.* At ordinary temperatures air has comparatively little action upon the metal, but when heated in the presence of air it burns with a brown flame, CdO being formed. It is soluble by heat in the mineral acids, hydrogen being evolved. The metal is precipitated by zinc from solutions of its salts. At a red heat cadmium vapor decomposes steam.

Uses.—Its presence in alloys reduces the fusing point of the alloy, without impairing the toughness or the malleability of the compound.

COMPOUNDS OF CADMIUM.

1. Cadmium oxide	CdO.
2. Cadmium hydrate	CdH_2O_2.
3. Cadmium chloride	$CdCl_2$.
4. Cadmium bromide	$CdBr_2$.
5. Cadmium iodide	CdI_2.
6. Cadmium sulphide	CdS.
7. Cadmium nitrate...	$Cd2NO_3,4H_2O$.
8. Cadmium carbonate	$CdCO_3$.
9. Cadmium sulphate	$CdSO_4$.

(1.) **Cadmium Oxide** ($CdO = 128$) is a brown powder, prepared either by burning the metal in air, or by igniting the nitrate. Insoluble in water, soluble in acids. Infusible at a white heat. Heated on carbon with the blowpipe, the metal is first reduced, the reduced metal afterwards volatilizing and burning, CdO being re-formed.

(2.) **Cadmium Hydrate** (CdH_2O_2) is formed by precipitating a cadmium salt with potassic hydrate. A white powder, insoluble in water or in solutions of sodic or potassic hydrate, but soluble in ammonia. It absorbs CO_2 from air.

(3.) **Cadmium Chloride** ($CdCl_2$). From a solution of the metal in HCl, crystals having the formula $CdCl_2,2H_2O$ may be obtained, from which the water may be driven off by heat. The anhydrous salt sublimes at a high temperature. Soluble in water (1·5 in 1 part of water at 60° F.).

(5.) **Cadmium Iodide** (CdI_2), is a salt used in photography.

(6.) **Cadmium Sulphide** ($CdS = 144$) (Greenockite), is precipitated in an amorphous form by H_2S or by an alkaline sulphide from a solution of a cadmium salt. When sulphur vapor is passed over very hot CdO, the sulphide may be obtained in crystals. Cadmium sulphide is employed as a bright yellow pigment, the color being remarkable for its purity and permanence. The yellow cadmium sulphide may be known from yellow orpiment by its non-volatility and insolubility in ammonic sulphide.

It is insoluble in nitric and in hydrochloric acids. It fuses at a white heat.

(9.) **Cadmium Sulphate** ($CdSO_4$) is deposited as crystals ($3CdSO_4,8H_2O$) from a solution of the oxide or carbonate in dilute sulphuric acid. It may be rendered anhydrous by heat. The anhydrous salt is soluble in water to the extent of 1 part in 2 parts of water at 60° F. By continuous heating, a basic sulphate ($CdO, CdSO_4H_2O$) is formed, which is not very soluble in water.

Reactions of Cadmium Compounds.

Flame.—No color.

Spectrum.—Characteristic lines in the red, green, and blue.

Alkaline hydrates.—A white ppt. (CdH_2O_2), insoluble in excess of KHO or NaHO, but soluble in ammonia.

Ammonium carbonate.—White ppt. ($CdCO_3$), insoluble in excess.

Sulphuretted hydrogen in HCl *solution.*—A yellow ppt. (CdS), insoluble both in ammonium sulphide (*see* Arsenic) and in potassic cyanide. Soluble in hot dilute H_2SO_4.

Blowpipe.—Heated on charcoal, cadmium salts yield a brown incrustation of CdO.

PALLADIUM (Pd″).

Atomic weight, 106·5. *Specific gravity,* 11·6. *Fusing point,* 2480° F., (1360° C.). *Atomicity, dyad* (″) *as in palladous compounds,* (*e.g.,* $PdCl_2$) ; *tetrad* (^{iv}) *as in palladic compounds* ($PdCl_4$).

History.—Discovered by Wollaston (1803).

Natural History.—Found in platinum ores (0·5 to 1 per cent.).

Extraction.—(*a.*) *Extraction from platinum ores.* After the platinum has been precipitated from its solution by ammonium chloride, the filtrate is neutralised, and the palladium precipitated as palladic cyanide with mercuric cyanide. This precipitate of palladic cyanide is collected and heated to redness, the spongy palladium thus obtained being afterwards heated, hammered, and welded.

A second method of effecting its separation from other metals is by precipitating a solution of palladous chloride with potassic iodide (avoiding excess), which throws down palladous iodide, to the exclusion of the other metals likely to be present. The iodide is then heated.

(*β.*) *Extraction from gold ores.*—The gold ore is first fused with silver. The fused mass is then boiled with nitric acid, whereby the gold separates as an insoluble precipitate. The silver in the solution is then precipitated with sodium chloride. The lead, copper, and palladium are precipitated together from the clear filtrate by placing a piece of metallic zinc in the liquid. The mixed precipitate thus obtained is then dissolved in nitric acid, from which the lead is precipitated by ammonia, leaving copper and palladium only in solution. The palladium is then precipitated by the addition of an excess of hydrochloric acid. This precipitate, when heated, leaves the pure metal.

Properties.—(*a.*) *Physical.* A hard, white, malleable and ductile metal, harder and lighter than platinum, although in many respects resembling it in appearance. Sp. gr. 11·6. It has been found crystallised in two forms (dimorphous), viz., in hexagons and octahedra. It is volatile at a high temperature, when it evolves a green vapor. At a red heat the metal absorbs oxygen, which it liberates on cooling. Spongy palladium will, like spongy platinum, determine the combination of oxygen and hydrogen. The metal possesses the property of absorbing many times its volume of hydrogen, giving it out again at high temperatures. This property is specially marked in the case of spongy palladium, which may be made to absorb 1000 times its volume of hydrogen, retaining 600 volumes at 212° F. (100° C.). Again, *hammered* palladium, which will absorb 640 times its volume of hydrogen, is far more powerfully absorbent than the *fused* metal, which only absorbs 68 times its bulk.—("Proceedings Royal Society," June, 1866.) At a high temperature the whole of the hydrogen absorbed at a low temperature is expelled. The specific gravity of the metal, saturated with hydrogen, is less than that of the metal free from absorbed hydrogen.

(β.) *Chemical.* Palladium is unaffected by sulphuretted hydrogen or by exposure to air at ordinary temperatures. At a low red heat the metal undergoes oxidation, the oxide formed being reduced at a higher temperature. It is soluble in nitric acid (forming palladous nitrate $Pd(NO_3)_2$), in hot sulphuric acid, and in hydrochloric acid in the presence of air or of chlorine. It is oxidized by fusion with the caustic alkalies, nitre, etc. It combines with iodine, forming palladous iodide (PdI_2). Hence, if an alcoholic solution of iodine be evaporated on palladium, a stain of PdI_2 is produced, a reaction which serves to distinguish palladium from platinum. If a wire of the metal be heated in the flame of coal gas or of a spirit lamp, it increases in size to many times its original volume, and becomes coated with cauliflower excrescences of a mixture of soot and palladium carbide. It decomposes ethylene with separation of carbon, at a temperature at which the gas is usually permanent. Its alloy with gold (1Pd and 4Au) is perfectly white and *brittle.* With silver (1Pd and 2Ag) it forms a white unoxidizable alloy of great ductility, and useful for small weights, its alloy with tin (1Pd and $8Sn = Pd_3Sn_2$) constituting a mixture remarkable for its great brilliancy.

The metal, saturated with hydrogen, is a powerful reducing agent, and will precipitate mercury and mercurous chloride when introduced into a solution of mercuric chloride.

Compounds of Palladium ($Pd = 106{\cdot}5$).

		COMPOUNDS.	Formulæ (General).	Molecular Weight.	Pd per cent.
1		Palladous hydride	Pd_2H		
2	Oxides.	Hypopalladous oxide	Pd_2O	229·0	93·01
3		Palladous oxide	PdO	122·5	86·93
4		Palladic ,,	PdO_2	138·5	76·89
5	Chlorides.	Palladous chloride	$PdCl_2$	177·5	60·00
6		Palladic ,,	$PdCl_4$	248·5	42·89
7		Palladous iodide	PdI_2	360·5	29·54
8		Palladous cyanide	$PdCy_2$	158·5	
9	Sulphides.	Hypopalladous sulphide	Pd_2S	245·0	
10		Palladous sulphide	PdS	138·5	
11		Palladic sulphide	PdS_2	170·5	62·46
12		Palladous nitrate	$Pd''2NO_3$		
13		,, sulphate	$PdSO_4 2H_2O$		

(1.) **Palladous Hydride** (Pd_2H). *Preparation.*—(1.) By heating the metal in hydrogen. (2.) By using a palladium pole as the negative electrode in the electrolysis of water.

Properties.—A metallic-like mass (Sp. gr. 11·06). When exposed to the air in a state of fine subdivision, it becomes red hot from oxidation of the hydrogen. When heated it gives up its hydrogen. It is a powerful reducing agent (*see* p. 471).

(2.) **Hypopalladous Oxide** or **Suboxide of Palladium** (Pd_2O) is prepared by heating palladous hydrate (PdH_2O_2) to redness. It is decomposed by acids.

(3.) **Palladous Oxide** (PdO) may be prepared either (*a.*) as a *brown hydrate* (PdH_2O_2) soluble in acids and in alkalies, by adding potassic carbonate to a palladous salt, or (*β.*) in an *anhydrous* form, by heating the hydrate, or by the ignition of the nitrate. By contact with hydrogen it is instantly reduced.

(4.) **Palladic Oxide** (PdO_2) is prepared as a yellowish-brown hydrate ($Pd^{iv}H_4O_4$) by acting on potassium palladic-chloride ($2KCl, PdCl_4$) with a solution of potassic hydrate. The anhydrous oxide may be obtained as a black powder by boiling the hydrate in water.

(5.) **Palladous Chloride**; *Chloride of Palladium* ($Pd''Cl_2 = 177·5$). *Preparation.*—(1.) By evaporating a solution of the metal in aqua regia (the metal being present in the solution as palladic chloride) to dryness.

(2.) By heating palladous sulphide in a current of dry chlorine.

Properties.—The hydrate is brown, and the anhydrous compound black. It is decomposed by heat, the metal being reduced. It forms double salts of a dark green color with the alkaline and other metallic chlorides (such as $PdCl_2,2KCl$). With ammonia, it forms a series of compounds similar to those formed by platinum. (*See* age 513.)

(6.) **Palladic Chloride** ($Pd^{iv}Cl_4$) is only known in solution. It forms double salts with the alkaline chlorides (as *e.g.*, the red and somewhat insoluble salt $2KCl,PdCl_4$). It is easily decomposed into palladous chloride and free chlorine.

(7.) **Palladous Iodide** ($Pd''I_2$).

Preparation.—By adding a soluble iodide to a soluble palladous salt. (The palladous iodide is soluble in excess of the soluble iodide.)

Properties.—A black substance, insoluble either in water or in ammonia, but soluble in an excess of potassic iodide. It is decomposed by a heat of 662° F. (350° C.).

[N.B.—In the laboratory, palladium salts are used for the estimation of iodine, since they do not precipitate either chlorine or bromine.]

(8.) **Palladous Cyanide** ($Pd''Cy_2$).

Preparation.—By the action of potassic or mercuric cyanide on neutral solutions of palladous salts.

Properties.—A yellow substance, soluble in ammonia, in acids, and in an excess of potassic cyanide.

(9.) **Hypopalladous Sulphide** (*subsulphide*), Pd_2S, is prepared by fusing palladous sulphide with a mixture of ammonic chloride, sulphur and potassic carbonate. Nitric acid has but little action upon it.

(10.) **Palladous Sulphide** ($Pd''S$) is formed by precipitating a palladous salt with sulphuretted hydrogen. It is insoluble in ammonic sulphide.

(11.) **Palladic Sulphide** is prepared by fusing the palladous sulphide with sodic carbonate, and decomposing the compound formed with hydrochloric acid.

Reactions of Palladium Compounds.

1. *Sulphuretted hydrogen;* a black ppt. ($Pd''S$), insoluble in ammonic sulphide. Soluble in boiling HCl.
2. *Mercuric cyanide;* a yellow ppt. ($Pd''Cy_2$) in neutral solutions.
3. *Potassic iodide;* a black ppt. ($Pd''I_2$), soluble in excess.
4. *Potassic and sodic hydrates;* a red or brown ppt., soluble in excess.
5. *Potassic and sodic carbonates;* a brown precipitate of $Pd''H_2O_2$ with palladous compounds.
6. *Ammonia and ammonic carbonates;* give with a solution of palladous chloride a flesh-colored ppt., soluble in excess of ammonia.
7. *Ferrous sulphate;* a black ppt. of metallic palladium.

Palladous salts are soluble, their solutions being either yellow or brown.

RHODIUM (Rh).

Atomic weight, 104. *Specific gravity,* 12·1. *Atomicity, dyad,* $Rh''O$; *tetrad,* RhO_2; *and pseudo-triad,* Rh_2O_3.

History.—Discovered by Wollaston (1803). Investigated by Berzelius and Claus.

Natural History.—Found in platinum ores (0·5 per cent.).

Extraction.—The excess of acid in the solution of the platinum ore in aqua regia, after extraction of the platinum (by NH_4Cl) and of the palladium (by mercuric cyanide) have been effected, is first of all neutralized. This neutral solution is now boiled with hydric sodic sulphite, when sodic rhodium sulphite ($Na_6Rh_26SO_3$) is precipitated. The metal may be obtained from a solution of this salt by reducing agents or by placing bars of zinc into the solution.

Properties.—(*a.*) *Physical.* A white hard metal (Sp. gr. 12·1), requiring a greater heat to fuse it even than platinum. It absorbs oxygen when melted.

(*β.*) *Chemical.*—It is oxidised when heated in air. If the metal be pure it is insoluble in acids, but it becomes soluble in nitro-hydrochloric acid, by alloying it with platinum, lead, etc., provided these latter metals be present in excess. It combines with sulphur by heat (RhS). It is dissolved when fused with potassic nitrate. By fusion with hydric potassic sulphate, a soluble potassium rhodic sulphate (K_2Rh2SO_4) is formed.

Compounds of Rhodium.

		COMPOUNDS.	Formulæ (General).
1	Oxides.	Rhodous oxide	RhO
2		Rhodium sesquioxide	Rh_2O_3
3		Rhodic oxide	RhO_2
4		,, chloride	Rh_2Cl_6
5		Rhodous sulphide	RhS
6		Rhodic sesquisulphide	Rh_2S_3
7		,, sulphite	$Rh_2(SO_3)_36H_2O$
8		,, sulphate	$Rh_2(SO_4)_312H_2O$
9		,, nitrate	$Rh_2(NO_3)_6$

The salts of the sesquioxide are those that have been chiefly studied.

Rhodic chloride (Rh_2Cl_6) is the only chloride known for certain. It is a red body, and forms double salts with alkaline chlorides. ($Rh_2Cl_6,6NaCl,24H_2O$).

Reactions of Rhodium Compounds.

Salts, rose-colored.

1. *Sulphuretted hydrogen;* a brown ppt. (possibly Rh_2S_3) in a hot solution, insoluble in ammonic sulphide.

2. *Soluble sulphides;* a pale yellow ppt.

3. *Potassic iodide;* a yellow ppt. (Rh_2I_6).

4. *Caustic alkalies;* a yellow ppt. ($Rh_2O_3,5H_2O$), soluble in acids and in excess of alkali.

5. Solutions of rhodic salts (which are usually rose-colored) are decomposed by iron or zinc, with precipitation of metallic rhodium.

6. The metal is reduced when heated in a current of hydrogen.

OSMIUM (Os).

[Mendeleef predicts that osmium has an atomic weight lower than that of iridium (193) instead of higher than that of gold (197).]

Atomic weight, 198·6. *Specific gravity,* 21·4. *Atomicity, dyad, tetrad and hexad.*

History.—Discovered by Smithson Tennant (1804), (ὀσμή, odor).

Natural History.—Is found in platinum ores, alloyed with iridium (osmiridium).

Extraction.—A mixture of osmiridium (*see* p. 474) with common salt is heated in a stream of *moist* chlorine. The $OsCl_4$ first formed, is decomposed by the water, OsO_4 (osmic acid) resulting, which being volatile, may be condensed in a receiver. The osmic acid solution is then precipitated with ammonia and ammonium sulphide, OsS_4 being formed. A mixture of osmic sulphide with sodic chloride, is now heated in a current of chlorine, and the mass treated with water. A solution of $OsCl_4,2NaCl$ is in this manner obtained. To this solution ammonic chloride is added, when a solution of $OsCl_4,2NH_4Cl$ results, which on being evaporated to dryness, and the residue ignited, yields metallic osmium.

Properties.—These vary. In a *state of powder*, rhodium is black, and has a specific gravity of 10. It is highly combustible, and is easily oxidised by nitric or by nitro-hydrochloric acid to OsO_4. In its *compact form* (*i.e.*, after ignition) it exhibits great lustre. It has a specific gravity of 21·4, and is not soluble in acids. In the *crystalline* state (*i.e.*, by fusing it with tin, and afterwards dissolving away the tin with hydrochloric acid), the metal has a specific gravity of 22·47, and is therefore the heaviest substance known. It is the least fusible of all the metals. A heat which fuses platinum, iridium and ruthenium, will not melt, although it may volatilise, osmium.

Compounds of Osmium (Os = 199).

		COMPOUNDS.	Formulæ (General.)	Molecular Weight.
1	Oxides.	Osmous oxide	OsO	215
2		Osmic sesquioxide	Os_2O_3	446
3		,, oxide	OsO_2	231
4		,, peroxide (osmic acid)	OsO_4	263
5	Chlorides.	Osmous chloride..	$OsCl_2$	270
6		Osmic sequichloride	Os_2Cl_6	611
7		,, chloride	$OsCl_4$	341
8		,, sulphide	OsS_4	327

(4.) **Osmic Peroxide.**—(*Osmic acid; Osmic anhydride*) (OsO_4) is formed when metallic osmium, or a lower oxide of osmium, is heated in air, or treated with aqua regia. It consists of colorless crystals, which are very volatile and intensely pungent. It fuses and boils at about 212° F. (100° C.). It is very soluble in water, the solution being neutral, staining the skin black, and possessing a strongly irritating smell. It is a powerful oxidising agent. It is soluble in alkalies, forming yellow solutions. Sulphuretted hydrogen precipitates a black sulphide (OsS_4) from alkaline solutions. The peroxide is precipitated from its solutions as a hydrate by alcohol and ether.

Osmates.—Neither osmic acid (H_2OsO_4) nor osmic anhydride have been prepared. Certain salts of osmic acid such as potassium and barium osmates (K_2OsO_4 ; $BaOsO_4$) have been obtained.

Osmic Sesquichloride (Os_2Cl_6) forms double salts, such as $Os_2Cl_6,6KCl,6H_2O$.

Osmic Chloride ($OsCl_4$). Prepared by heating the metal in dry chlorine. A red volatile body, soluble in water.

REACTIONS OF OSMIUM COMPOUNDS.

1. Osmium compounds yield a peculiar odor when heated with nitric acid.

2. *Sulphuretted hydrogen*, when passed through a solution of OsO_4 acidulated with HCl, gives a black ppt. (OsS_4), which is very slightly soluble in ammonic sulphide.

Reactions of Osmic Acid:—

1. *Potassic nitrite;* produces a red salt, *viz.*, potassium osmite.
2. *Sodic sulphite;* produces a blue salt, *viz.*, osmium sulphite.

RUTHENIUM (Ru).

Atomic weight, 104·4. *Specific gravity of the porous metal*, 8·6, *and of the fused metal*, 11·4. *Atomicity, dyad* ($RuCl_2$), *and tetrad* ($RuCl_4$).

History.—Discovered by Claus (1846).

Natural History.—Found in platinum ores. Also as a sulphide in the mineral "laurite," together with sulphide of osmium (Borneo).

Extraction.—When platinum ore is acted upon with aqua regia, an insoluble white scaly residue remains, consisting of an alloy of osmium, iridium, and ruthenium, with a little rhodium. When this residue is heated in a current of air, the osmium is oxidised (OsO_4) and volatilises, the vapor being condensed either in flasks or in a solution of caustic potash. The osmic acid vapor, moreover, carries over the ruthenium mechanically mixed with it, as ruthenic oxide, the RuO_2 not being itself volatile. This may be collected on fragments of porcelain placed in immediate contact with the heated tube. Metallic ruthenium may be prepared from this oxide by heating in hydrogen. Ruthenium and iridium are also found in the residue remaining in the tube. By fusing this residue with potassic hydrate, a soluble potassic ruthenate (K_2RuO_4) is produced, from a solution of which Ru_2O_3 may be precipitated by nitric acid, and the oxide formed reduced by ignition in hydrogen.

Properties.—(*a.*) *Physical.* A hard, brittle, and almost infusible metal. Specific gravity, 12·3.

(*β.*) *Chemical.* Undergoes oxidation with difficulty when heated in air, but with readiness when heated with potassic hydrate or with potassic nitrate, a potassic ruthenate being formed. This salt, dissolved in water, yields a yellow-colored solution.

Compounds of Ruthenium.

	COMPOUNDS.		Formulæ (General).	Molecular Weight.
1	Oxides.	Ruthenous oxide	RuO	120·4
2		Ruthenic sesquioxide	Ru_2O_3	256·8
3		,, oxide	RuO_2	136·4
3A		,, hydrate	RuH_4O_4	
4		,, peroxide	RuO_4	168·4
5	Chlorides.	Ruthenous chloride	$RuCl_2$	175·5
6		Ruthenic sequichloride	Ru_2Cl_6	421·8
7		,, chloride	$RuCl_4$	246·4
8		,, sesqui-iodide	Ru_2I_6	
9		,, sesquisulphide	Ru_2S_3	304·8
10		,, sulphate	$Ru2SO_4$	

Oxides.—*Ruthenous oxide* (RuO) is a dark grey powder, not affected by acids. *Ruthenic sesquioxide* (Ru_2O_3) and *ruthenic oxide* (RuO_2) are feeble bases.

Ruthenic Peroxide (RuO_4) is prepared by passing chlorine through a solution of potassic ruthenate, when the RuO_4 volatilizes as a yellow crystalline body. The crystals fuse at 104° F. (40° C.), and boil at 212° F. (100° C.).

Ruthenates.—*Salts of ruthenic acid* (H_2RuO_4). Neither the acid nor its anhydride (RuO_3) have been prepared. Certain ruthenates (*e.g.*, *potassium ruthenate,* K_2RuO_4, formed by fusing the finely dissolved metal with caustic potash and nitre) are known.

Perruthenates.—Salts of perruthenic acid ($HRuO_4$). Certain salts (such as *potassium perruthenate,* $KRuO_4$, formed by the action of chlorine on the ruthenate) are known.

The Chlorides.—*Ruthenous chloride* ($RuCl_2$) is prepared by heating the metal in a current of chlorine. It is insoluble in acids. *The sesquichloride* (Ru_2O_3) forms double chlorides with alkaline chlorides. *Ruthenic chloride* ($RuCl_4$) is formed by dissolving ruthenic hydrate in hydrochloric acid. It also forms double chlorides with alkaline chlorides. Ammonium compounds of ruthenium have been prepared.

Reactions of Ruthenium Compounds.

Dissolve the residue formed by fusing caustic potash with a ruthenium compound, in water. Test the solution as follows :—

1. *Nitric acid;* a black ppt. (Ru_2O_3).

2. Add *hydrochloric acid* to the liquid holding the Ru_2O_3 (formed by re-action No. 1) in suspension. On applying heat, an orange yellow solution results.

3. Treat this solution with *sulphuretted hydrogen*; a black ppt. results, the filtrate presenting a blue color.

4. *Plumbic acetate;* a purple red ppt.

B. METALS WHOSE SULPHIDES ARE SOLUBLE IN THE ALKALINE SULPHIDES.

TIN (Sn).

Atomic weight, 118. *Specific gravity,* 7·28. *Fusing point,* 442·4° F. (228° C.). *Boils at about* 2912° F. (1600° C.). *Specific heat,* 0·0562. *Atomicity, dyad, as in stannous compounds* (*as* $Sn''O$; $Sn''Cl_2$) ; *and tetrad, as in stannic compounds* ($Sn^{iv}O_2$; $Sn^{iv}Cl_4$).

History.—The metal was known to the ancients (*Stannum*).

Natural History.—Found as "tin stone," or *cassiterite* (SnO_2), in veins in the granite and quartz (mine-tin). Also found in small round nodules in alluvial soils (stream-tin ore). It is commonly associated with arsenical iron pyrites, and with manganese and iron oxides. It also occurs along with tungstic anhydride (WO_3) in the mineral called "wolfram." It rarely occurs free.

Preparation.—(*α.*) The ore is first crushed, and afterwards washed, to remove foreign matters (Sp. gr. of quartz 2·7 ; Sp. gr. of SnO_2, 6·5).

(*β.*) The washed ore is then *roasted,* by which means the arsenicum (as As_2O_3) and the sulphur (as SO_2) present in the ore are expelled. The iron after roasting exists in the ore as Fe_2O_3, and the copper chiefly as sulphate. To effect complete conversion of the sulphide into sulphate of copper, the roasted ore is first of all damped with water, and then exposed to the air for some days.

(*γ.*) The mass is now treated with water. By this means the cupric sulphate is dissolved out, and much of the ferric oxide mechanically washed away, owing to the specific gravity of the ferric oxide being less than that of stannic oxide.

(*δ.*) The residual tin ore is now *reduced.* This is effected by mixing it with powdered coal and a little lime, and heating the mixture in a reverberatory (reducing) furnace ($SnO_2+C_2=Sn+2CO$). The *coal* reduces the SnO_2, carbonic oxide being evolved, the *lime* forming a fusible slag with the earthy impurities.

(*ε.*) The reduced metal has then to be *refined,* crude tin containing iron, arsenic, copper and tungsten. The metal is first of all heated, when the purer portions, being more fusible than the alloy, melt first, and are allowed to run off into moulds (*block tin*), leaving the less fusible and less pure alloy behind. The purity of the tin is roughly known by its breaking into irregular prismatic fragments (dropped or grain tin) when the hot ingots are struck with a hammer.

Properties.—(*α.*) *Physical.* A white metal, soft and malleable, but not ductile, unless heated to 212° F. (100° C.). At 392° F. (200° C.) it becomes brittle. It is very wanting both in tenacity and elasticity. It crackles when bent from the friction and breaking of the crystals, considerable heat being developed. Its smell when rubbed is peculiar. It may be made to crystallise by slow cooling. Its crystalline character is well shown in the *moirée métallique,* prepared by washing tin plate with dilute nitro-hydrochloric acid. It fuses at 442° F. (227° C.), but is not volatile. It is a good conductor of heat and electricity.

(β.) *Chemical.* At ordinary temperatures tin is unacted upon either by air or by water, singly or conjointly. When melted, it undergoes superficial oxidation. It burns in air at a high temperature, with a white light, forming "putty powder" (SnO_2). It decomposes steam at a red heat, an oxide of the metal being formed.

Action of Acids.—Strong nitric acid (Sp. gr. 1·5) has no action upon the metal, but dilute nitric acid (Sp. gr. 1·3) forms with it the white insoluble metastannic acid ($H_2Sn_5O_{11},4H_2O = 5H_2SnO_3$) and ammonia. With still more dilute nitric acid *stannous nitrate* ($Sn2NO_3$) and *stannic nitrate* ($Sn4NO_3$) are formed, stannic nitrate rapidly decomposing, a gelatinous precipitate of hydrated stannic acid (H_2SnO_3) being precipitated. When strong sulphuric acid is boiled with the metal, it converts it into stannous sulphate, sulphurous acid being evolved with separation of sulphur, the latter probably resulting from the stannous sulphate becoming oxidised to stannic sulphate, at the expense of the oxygen of the sulphurous anhydride ($Sn + 2H_2SO_4 = SnSO_4 + SO_2 + 2H_2O$). Dilute sulphuric acid has no action upon it. Strong hydrochloric acid dissolves the metal when heated with it, hydrogen being evolved and stannous chloride formed ($Sn + 2HCl = SnCl_2 + H_2$). The metal is soluble in aqua regia, when stannic chloride ($SnCl_4$) results.

The fixed alkaline hydrates, when heated in contact with tin, dissolve it, hydrogen being evolved, and an alkaline stannate formed ($Sn + 2KHO + H_2O = K_2SnO_3 + 2H_2$). Tin combines readily by heat with sulphur, with phosphorus, and with the haloids.

Impurities.—Lead, iron, copper, arsenic, antimony, bismuth, gold and tungsten.

Uses.—For *Tin-foil. Tin plate* consists of iron coated with tin. The iron (the positive element), after being freed from adherent oxide by immersion in acids and subsequent scouring and washing, is dipped into melted tin (the negative element). Sometimes after dipping the plate is hammered, in order to effect the more perfect union of the tin and iron (block tin). If the covering of the tin be imperfect, the corrosion of the iron is rendered more rapid, a galvanic couple being formed which decomposes the water, the oxygen from which rusts the iron. In *tinning copper vessels,* any oxide on the copper is first removed by rubbing it over with ammonium chloride and heating ($CuO + 2NH_4Cl = CuCl_2 + H_2O + 2NH_3$), the clean and hot surface being afterwards rubbed with melted tin.

Pins are made from brass wire, tinned by boiling in water containing cream of tartar, alum, sodic chloride and granulated tin. An acid solution of tin is formed, from which the tin is thrown down on the brass by electrolytic action.

Tin forms an important ingredient of many alloys, as, *e.g.*, *Britannia metal* (Brass, Sn, Sb, equal proportions) ; *pewter* (Sn, Pb) ; *speculum metal* (Cu, Sn, a little As) ; *bell metal, gun metal and bronze* (Cu, Sn) ; *bronze coin* (Cu, Sn, Zn) ; *type metal* (Sn, Sb, Pb) ; *solder*, such as *fine solder* (2Sn and 1Pb), *common solder* (1Sn and 1Pb), *coarse solder* (1Sn and 2Pb). An *amalgam of tin* is used for silvering mirrors.

Compounds of Tin (Sn = 118).

	COMPOUNDS.	Formulæ (General).	Molecular Weight.	Sn per cent.
1	Stannous oxide	$Sn''O$	134	88·06
2	,, hydrate	SnH_2O_2		
3	Sesquioxide	Sn_2O_3		
4	Stannic oxide	SnO_2	150	78·66
5	,, hydrate	SnH_4O_4		
6	Metastannic acid	$H_2Sn_5O_{11},4H_2O$	840	70·23
7	Stannic acid	H_2SnO_3	168	
8	Stannous chloride	$SnCl_2$	189	62·43
9	Stannic chloride	$SnCl_4$	260	45·38
10	Stannous oxychloride	Sn_2OCl_2		
11	,, bromide	$SnBr_2$		
12	Stannic ,,	$SnBr_4$		
13	Stannous iodide	SnI_2		
14	Stannic ,,	SnI_4		
15	Stannous fluoride	SnF_2		
16	,, sulphide	SnS	150	78·66
17	Sesquisulphide	Sn_2S_3		
18	Stannic sulphide	SnS_2	182	
19	Stannous sulphate	$SnSO_4$		
20	Stannic ,,	$Sn2SO_4$		

COMPOUNDS OF TIN AND OXYGEN, ETC.

1. Stannous oxide ... ... SnO.
2. Stannous hydrate ... ... SnH_2O_2.
3. Sesquioxide of tin (stannous stannate) Sn_2O_3.
4. Stannic oxide ... ... SnO_2.
5. Stannic hydrate ... ... SnH_4O_4.
6. Metastannic acid ... $5SnO_2,5H_2O=H_2Sn_5O_{11},4H_2O$.
7. Stannic acid ... ... $SnO_2,H_2O=H_2SnO_3$.

(1 and 2.) Stannous Oxide (SnO) and Stannous Hydrate (SnH_2O_2).

Preparation.—(1.) (*As a hydrate.*) By adding an excess of an alkaline carbonate to a solution of stannous chloride, CO_2 being evolved.

(2.) (*Anhydrous.*) (*a.*) By igniting the hydrate in nitrogen or in carbonic anhydride.

(*β.*) By heating stannous oxalate in closed vessels. (If heated in the open air SnO_2 is formed.)

Properties.—The hydrate is a white body absorbing oxygen freely from the air. It is soluble when heated in a strong solution of potassic hydrate, forming *potassium stannite* ($K_2O,2SnO=K_2Sn_2O_3$), but if the boiling be long continued, or if the solution be kept for some time, the metal is precipitated, SnO_2 (or *potassium stannate,* $K_2O,SnO_2=K_2SnO_3$) remaining in solution. It is soluble in acids. With sulphuric acid it forms stannous sulphate ($Sn''SO_4$).

The anhydrous stannous oxide is a black body, permanent in air, but burns like tinder when ignited, forming stannic oxide (SnO_2).

It will therefore be noted that stannous oxide may act (*a.*) as a *basic* oxide, its salts being called *stannous salts,* in which the tin plays the part of a dyad (*e.g.* $Sn''SO_4$, *stannous sulphate*), and also (*β.*) as a weak *acid* (*e.g.,* K_2O, $2SnO$, *potassium stannite*).

(3.) **Sesquioxide of Tin** (Sn_2O_3) is known.

(4.) **Stannic Oxide.**—*Binoxide of tin* (SnO_2) is found native as tin-stone. It is a white powder when cold, and yellowish brown when hot. It is formed whenever the hydrates or the metal or stannous oxide are ignited in air. It is insoluble in acids, except in sulphuric acid, but forms soluble compounds when boiled with the alkalies. It forms two hydrates, both of which are acids.

Stannic oxide may act (*a.*) as a *basic* oxide, its salts being called *stannic salts,* in which the tin plays the part of a tetrad (*e.g.* $Sn^{iv}(SO_4)_2$, *stannic sulphate*), and (*β.*) as an *acid* in the form of its two hydrates, metastannic and stannic acids.

(6.) (*a.*) **Metastannic Acid.**—A compound having the formula ($5SnO_2,10H_2O$) results when tin is treated with nitric acid. When this product is dried at 212° F. (100° C.) it becomes $5SnO_2,5H_2O$, a white powder insoluble either in water or in acids. By the further action of heat upon this hydrate, it changes to a yellow color (probably becoming anhydrous), forming what is called "putty powder," a subtance used to polish plate. The acid forms non-crystallisable salts called "*metastannates,*" in which one-fifth part of the hydrogen of the acid is replaced by a metal—

$$\left[\left.\begin{matrix}K_2O\\4H_2O\end{matrix}\right\}(SnO_2)_5\right].$$

Hence we regard $H_2Sn_5O_{11},4H_2O$ as the formula for metastannic acid.

(7.) (*β.*) **Stannic Acid** ($SnO_2,H_2O=H_2SnO_3$) is formed when an alkali is added to a solution of stannic chloride. It is soluble in acids. It is also soluble in cold solutions of potassic and sodic hydrates, forming crystallisable salts called "*stannates*," in which the whole of the hydrogen of the acid is exchanged for the metal (*e.g.*, sodium stannate, $SnO_2,Na_2O = Na_2SnO_3$).

Sodium Stannate ($Na_2SnO_3,4H_2O$) forms the "Tin Prepare Liquor" of the calico-printer.

COMPOUNDS OF TIN AND THE HALOIDS.

8. Stannous chloride ... ... $SnCl_2$.
9. Stannic chloride; (Bromide) ... $SnCl_4$; ($SnBr_4$).
10. Stannous oxychloride ... ... Sn_2OCl_2.

(8, 10.) **Stannous Chloride.**—*Protochloride of tin; "Tin salt;"* ($SnCl_2$).

Preparation.—(1.) (*As a hydrate*, $SnCl_2,2H_2O$.) By dissolving tin in hydrochloric acid, and evaporating the solution until it crystallises.

(2.) (*Anhydrous*, $SnCl_2$.) (*a.*) By heating the hydrate to 212° F. (100° C.).

(β.) By heating tin filings with mercuric chloride ($Sn + HgCl_2 = SnCl_2 + Hg$).

Properties.—A white crystalline body, the hydrate being soluble in about one-third its weight of water. (See below for the action of an excess of water.) Sp. gr., 2·7. Its composition at 1292° F. (700° C.) corresponds to the formula Sn_2Cl_4 (molecular weight 376), but at higher temperatures to $SnCl_2$ (molecular weight 189). Fuses at 482° F. (250° C.). Boils at 1148° F. (620° C.). At a high temperature undergoes decomposition. It has a strong attraction both for chlorine and oxygen, absorbing the latter from the air, whether exposed to it in a solid or dissolved state, a mixture of stannic chloride and stannous oxychloride being formed. Hence the use of stannous chloride as a reducing agent;—dechlorinating chlorides ($SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$);—deoxidising salts of mercury, silver and gold;—converting ferric and cupric salts into ferrous and cuprous salts;—depriving sulphurous acid of its oxygen (a yellow precipitate of stannic sulphide being thrown down);—deoxidising indigo;—reducing combined metallic acids (such as CrO_3, As_2O_5, etc.) to a lower state of oxidation, etc. When mixed with a large quantity of water, stannous chloride is decomposed, and a basic salt precipitated (SnO,HCl). If this mixture be exposed to the air, a white hydrated oxychloride is formed ($2SnCl_2 + H_2O = Sn_2OCl_2 + 2HCl$).

Stannous chloride forms double crystallizable chlorides.

Stannous chloride constitutes the "tin crystals," or "salts of tin," of the dyer. It is commonly dissolved for use in a copper vessel, its solubility being increased by the resulting voltaic action.

(9.) **Stannic Chloride** ($SnCl_4$).—*Bichloride and tetrachloride of tin; fuming liquor of Libavius; butter of tin; oxymuriate of tin.*

Preparation.—(1.) By passing chlorine over fused metallic tin.

(2.) By distilling together powdered tin (1 part) and mercuric chloride (4 parts) ($2HgCl_2 + Sn = SnCl_4 + Hg_2$).

Properties.—The anhydrous salt is a thin, colorless fuming liquid, boiling at 239·5° F. (115·3° C.). Sp. gr. 2·234 at 50° F. (10° C.). It has a vapor density of 9·2. When mixed with a little water, it solidifies to a soft mass called "butter of tin" ($SnCl_4,3H_2O$), but it also forms hydrates with 5 and 8 molecules of water. On adding an excess of water to stannic chloride, hydrated stannic acid is thrown down, and hydrochloric acid set free. It forms numerous double salts with metallic chlorides called *chloro-stannates* (as *e.g.*, the "pink salt" of the dyer, $2NH_4Cl,SnCl_4$). Stannic chloride is largely used by dyers (called nitro-muriate of tin) for the purpose of fixing and brightening red colors.

(**11** to **15.**) Stannic and stannous bromide ($SnBr_2$ and $SnBr_4$), the corresponding iodine compounds (SnI_2 and SnI_4), and stannous fluoride (SnF_2), have been prepared—the stannous compounds, by the action of the hydracid on tin, and the stannic compounds by the direct union of tin with the haloid element. No stannic fluoride has been prepared, but from the existence of the *stannico-fluorides* (*e.g.*, K_2F_2,SnF_4) such a compound may be assumed to exist.

COMPOUNDS OF TIN AND SULPHUR.

16.	Stannous sulphide	SnS.
17.	Sesquisulphide of tin (stannous sulphostannate)	Sn_2S_3.
18.	Stannic sulphide...	SnS_2.

(**16.**) **Stannous Sulphide.**—*Protosulphide of tin* (SnS). Found native as "tin pyrites."

Preparation.—(1.) (*Anhydrous.*) By fusing together tin and sulphur.

(2.) (*As a hydrate.*) By passing sulphuretted hydrogen through a solution of a stannous salt ($SnCl_2 + H_2S = SnS + 2HCl$).

Properties.—A blackish grey body, soluble in hot hydrochloric acid ($SnS + 2HCl = SnCl_2 + H_2S$) and in yellow ammonium sulphide. The *sulpho-stannates* (M'_2SnS_3) are formed by the action of an alkaline disulphide on stannous sulphide, from which solutions stannic acid is precipitated on the addition of acids.

(**17.**) **Sesquisulphide of Tin** (Sn_2S_3) (*stannous sulphostannate*) is prepared by heating stannous sulphide with one-third its weight of sulphur.

(**18.**) **Stannic Sulphide.**—*Disulphide of tin ; mosaic gold* (a crystalline sulphide) ; *bronze powder* (SnS_2).

Preparation.—(1.) (*Anhydrous.*) By heating together, at a low red heat, tin (12 parts), mercury (6 parts), ammonium chloride (6 parts) and sulphur (7 parts), the stannic sulphide subliming.

(2.) (*As a hydrate.*) By passing sulphuretted hydrogen through an acid solution of a stannic salt.

Properties.—A yellow-colored body, used in the arts as an imitation of gold or bronze. It is decomposed by heat into stannous sulphide (SnS) and free sulphur. It is soluble in solutions of the alkaline hydrates and sulphides when heated, and also in aqua regia, but is insoluble in nitric or in hydrochloric acids.

Sulpho-stannates are also formed by dissolving stannic sulphide in solutions of the alkaline polysulphides (*see above*).

REACTIONS OF THE COMPOUNDS OF TIN.

(A.) STANNOUS SALTS :—

(1.) In solution, stannous salts absorb oxygen and become stannic salts.

(2.) *Caustic alkalies* precipitate SnH_2O_2 ; ppt. soluble in excess. On boiling, a portion of the metal separates and an alkaline stannate remains in solution.

(3.) *Ammonia;* ppt. of SnH_2O_2, insoluble in excess.

(4.) *Alkaline carbonates* (ppt. similar to that produced by ammonia).

(5.) *Sulphuretted hydrogen.* A dark brown ppt. of SnS in acid or neutral solutions.

(6.) *Auric chloride* gives a purple precipitate (Purple of Cassius) in solutions of stannous chloride containing a small quantity of stannic chloride.

(7.) *Mercuric chloride.* A white ppt. with stannous chloride of Hg_2Cl_2, which on heating becomes grey from the formation of metallic mercury.

(B.) STANNIC SALTS :—

(1.) *Caustic alkalies.* A white precipitate of H_2SnO_3, soluble in excess.

(2.) *Sulphuretted hydrogen.* A yellow precipitate of SnS_2 soluble in alkalies and in alkaline sulphides.

TITANIUM (Ti).

Atomic weight, 48. *Specific gravity*, 5·3. *Atomicity, dyad in titanous compounds* ($TiCl_2$), *and tetrad in titanic compounds* ($TiCl_4$).

History.—Discovered by Gregor (1791). [*Titan*, a son of the earth.]

Natural History.—It is never found free, but occurs as $Fe_2Ti_2O_3$ in titaniferous iron (*iron sand*) ; also as titanic anhydride (TiO_2) in rutile, anatase, brookite, etc.

In iron furnaces certain crystals are frequently found adhering to the slag, and consist of a mixture of cyanide and nitride of titanium ($TiCy_2,3Ti_3N_2$) (Wöhler). These crystals are extremely hard, almost absolutely infusible, and have a specific gravity of 5·3. They are insoluble in any acid, except in a mixture of nitric and hydrofluoric acids.

Preparation.—(1.) By heating titanic oxide (TiO_2) with charcoal.

(2.) By heating sodium in the vapor of titanic chloride.

(3.) By heating potassium titano-fluoride ($TiF_4,2KF$), with potassium.

Properties.—A dark green substance. Specific gravity 5·3. It burns with vivid scintillations in air and oxygen, and in burning absorbs both oxygen and nitrogen. Hydrochloric acid dissolves it, with the evolution of hydrogen. It possesses great affinity for nitrogen.

Compounds of Titanium (Ti = 48).

	COMPOUNDS.	Formulæ (Common).	Molecular Weight.
1	Titanous oxide	TiO	64
2	Sesquioxide of titanium..	Ti_2O_3	144
3	Titanic oxide (anhydride)	TiO_2	80
4	Titanic acid	TiO_2,H_2O	98
5	Titanous chloride	$TiCl_2$	119
6	Titanic chloride	$TiCl_4$	190
7	Ditanic hexafluoride	Ti_2F_6	210
8	Titanic fluoride	TiF_4	124
9	Titanic sulphide	TiS_2	112
10	Titanic nitrides	TiN_2 Ti_2N_6 Ti_5N_6	76
11	Titanic cyano-nitride	Ti_5N_3Cy	

COMPOUNDS OF TITANIUM AND OXYGEN, ETC.

Titanous oxide	TiO.
Sesquioxide of titanium	Ti_2O_3.
Titanic oxide (or anhydride) ...	TiO_2.
Titanic acid ...	$(H_2TiO_3)=TiO_2,H_2O$.

(1.) **Titanous Oxide.**—*Protoxide of titanium* (TiO) is a black powder, and may be obtained by heating TiO_2 in a crucible lined with charcoal (?), or as a hydrate by adding ammonia to a solution of a titanous salt. On boiling this precipitate in the solution, titanic acid is formed.

(2.) **Sesquioxide of Titanium** (Ti_2O_3) is obtained as a dark brown powder by igniting titanic anhydride in a current of hydrogen. It rapidly absorbs oxygen from the air.

(3 and 4.) **Titanic Oxide.**—*Dioxide; titanic anhydride; titanic acid* (TiO_2). This body occurs native as rutile (*Specific gravity*, 4·25; *Crystals, brown needle-prisms*), anatase, (*Specific gravity*, 3·9; *Crystals*,

blue transparent octahedra), and brookite (*Specific gravity*, 4·13; *Crystals, right rhombic prisms*). It also occurs in combination with oxide of iron (iron sand).

Preparation.—(1.) Powdered "rutile," or "iron sand," is first fused with potassic carbonate. After the fused mass has been treated with hot water, the residue (an acid potassic titanate) is dissolved in hydrochloric acid, and the solution evaporated to dryness. In this way the titanic oxide with any silica present are converted into their insoluble modifications. The residue is now fused with acid potassic sulphate, whereby a yellow mass is obtained having the composition TiO_2,SO_3, and which, being soluble, may be separated from the silica by treatment with cold water. On boiling this solution, titanic oxide is precipitated as a white powder.

(2.) Titanic acid may be prepared by adding ammonia to a solution of titanic chloride, when $TiO_2,2H_2O$ is precipitated, which on drying in vacuo, becomes TiO_2, H_2O. At a higher temperature the anhydride (TiO_2) will be formed.

Properties.—Titanic oxide (anhydride) is a white powder, which on ignition becomes *black*. It is insoluble in all acids, except in hydrofluoric and boiling sulphuric acids. Fused with potassic carbonate it forms a yellow potassic titanate, which is soluble in hydrochloric acid, and from which solution titanic oxide may be precipitated as a hydrate on adding ammonic carbonate.

If a mixture of charcoal and titanic anhydride be heated, and whilst hot introduced into a jar of nitrogen, the nitrogen will be absorbed and CO formed. If ammonia gas be passed over red-hot titanic anhydride, the violet titanium dinitride (TiN_2) is formed.

Titanic acid (*hydrate*) is yellow when hot and white when cold. It is soluble in hydrochloric and sulphuric acids, thus distinguishing it from silica. It is insoluble in a solution of potassic hydrate, but forms a titanate when fused with potash. This potassium titanate is decomposed by water, an acid potassic titanate being formed which is soluble in hydrochloric acid, from which solution hydrated titanic acid (TiO_2,H_2O) may be precipitated by ammonia. Our knowledge of the titanates is imperfect. The normal salts are insoluble in water.

Probably the hydrates of titanic oxide are analogous to the hydrates of stannic oxide, viz., titanic and meta-titanic acids (*see* page 481).

Compounds of Titanium and Chlorine.

5.	Titanous chloride	$TiCl_2$.
6.	Titanic chloride	$TiCl_4$.

(5.) **Titanous Chloride** ($TiCl_2$) forms lustrous violet-colored crystals, and may be prepared by heating titanic chloride in hydrogen.

The solution of the salt, which at first is violet-colored, becomes colorless on exposure to air.

(6.) **Titanic Chloride.**—*Tetrachloride of titanium* ($TiCl_4$) is prepared by passing chlorine over a red-hot mixture of titanic oxide and charcoal ($TiO_2 + 2C + 2Cl_2 = TiCl_4 + 2CO$). It is a volatile, fuming, colorless liquid (Sp. gr. of vapor, 6·836 ; of liquid, 1·761 at 32° F.). It boils at 275° F. (135° C.). It is decomposed by an excess of water, titanic acid being precipitated.

(9.) **Titanic Sulphide** (TiS_2) is formed as a yellow solid when the vapor of $TiCl_4$ mixed with H_2S is passed through a red-hot tube.

(10, 11, 12.) **Titanic Nitride** (TiN_2) is a dark powder formed by heating TiO_2 in a current of nitrogen. The nitride Ti_3N_4 is formed by heating the compound $TiCl_4,4NH_3$ in a current of gaseous ammonia, and the nitride Ti_5N_6 by heating Ti_3N_4 in hydrogen. The cyano-nitride Ti_5N_3Cy is found in blast furnaces that have been used for smelting titaniferous iron. [*See* reference under Natural History of Titanium.] Both the cyano-nitride and the nitrides were formerly mistaken for metallic titanium.

REACTION OF TITANIUM COMPOUNDS.

(A.) TITANOUS COMPOUNDS. (Titanous salts only known in solution.)

Ammonium Carbonate.—A black ppt., changing to blue, then to brown, and finally to green.

(B.) TITANIC COMPOUNDS. (Titanic acid and alkaline titanates are insoluble in water, but soluble in HCl.)

(1.) *Ammonia ;* a white ppt.

(2.) *Infusion of galls ;* an orange-colored ppt.

(3.) *Potassic ferrocyanide ;* a brown ppt.

(4.) The *borax* or *microcosmic bead*, gives with titanium oxide in the inner blowpipe flame a yellow bead when hot, changing to violet on cooling.

ANTIMONY (Sb).

Atomic weight, 122. *Molecular weight* (*probable*), 488. *Specific gravity* (*amorphous*), 5·7; (*crystalline*), 6·7. *Fusing point*, 842° F. (450° C.). *Boils between* 1100° *and* 1450° C. *Specific heat*, 0·0508. *Atomicity, a triad in antimonious compounds* ($SbCl_3$; Sb_2O_3), *and a pentad in antimonic compounds* ($SbCl_5$; Sb_2O_5).

History.—Discovered by Basil Valentine (15th century).

Natural History.—It is found native, but more commonly occurs as *stibnite* or *grey antimony ore* (Sb_2S_3). Also found as *valentinite* (Sb_2O_3) and as antimony ochre.

Preparation.—(A.) *Crystalline Form.* (1.) By melting out the antimony (owing to its ready fusibility) from the metals with which it is alloyed (*crude antimony*).

(2.) (*a.*) The ore (Sb_2S_3) is first *roasted*, in order to drive off some of the sulphur and arsenic present:—

(*β.*) This roasted ore, which consists of a mixture of oxide (Sb_2O_3) and sulphide (Sb_2S_3), is now fused with charcoal and sodic carbonate (*regulus of antimony*). The sodic carbonate converts any sulphide present into oxide ($Sb_2S_3 + 3Na_2CO_3 = 3CO_2 + 3Na_2S + Sb_2O_3$), whilst the carbon reduces the oxide to the metallic state ($Sb_2O_3 + 3C = 3CO + Sb_2$).

(3.) By fusing Sb_2S_3 with iron filings ($Sb_2S_3 + 3Fe = 3FeS + Sb_2$).

(B.) *Amorphous Form.* This variety is formed when a solution of tartar emetic in antimonious chloride is subjected to electrolysis.

Properties.—(*a.*) *Physical.* A bluish-white, brittle metal, occurring both in a crystalline (*rhombohedra*) and amorphous condition. It fuses at 842° F. (450° C.), and is volatile at a bright red heat, when it may be distilled. Contrary to the general rule, antimony expands on solidifying. Its power of conducting heat and electricity is comparatively small. The amorphous variety on heating undergoes a molecular change into ordinary antimony, the conversion being attended with a considerable rise of temperature.

(*β.*) *Chemical.*—At ordinary temperatures antimony is unacted upon by the air, but when very strongly heated in air it burns, forming Sb_2O_3 (antimonious oxide). It fuses and fires when thrown into chlorine, and also combines with bromine and iodine, with the evolution of great heat. With hot sulphuric acid it yields antimonious sulphate, sulphurous anhydride being evolved ($2Sb + 6H_2SO_4 = Sb_2(SO_4)_3 + 3SO_2 + 6H_2O$). Nitric acid oxidises it to antimonic anhydride (Sb_2O_5), which is insoluble in the acid. It readily dissolves by heat in aqua regia, $SbCl_3$ or $SbCl_5$ being formed according to the amount of acid employed. It is also soluble when heated in hydrochloric acid, hydrogen being evolved and $SbCl_3$ formed. It is soluble in potassic sulphide.

Uses.—It is used in the preparation of several alloys, such as *type metal* (2Pb, 1Sn, and 1Sb), a compound that expands slightly on cooling, thus rendering the cast sharp; *Britannia metal* (9Sn, 1Sb); *pewter* (12Sn, 1Sb, and Cu), etc. It is used in medicine.

Compounds of Antimony ($Sb = 122$).

		COMPOUNDS.	Formulæ (General).	Molecular Weight.	Specific Gravity.	Sb per cent.
1		Antimoniuretted hydrogen ..	SbH_3	125·0		97·60
2		Antimonious oxide	Sb_2O_3	292·0	5·2	83·56
3	Oxides.	Metantimonious acid	$HSbO_2$			
4		Antimonious antimoniate ..	Sb_2O_4	304		
5		Antimonic oxide	Sb_2O_5	325	5·6	
6		Antimonic acid	$HSbO_3$			
7		Metantimonic acid	$H_4Sb_2O_7$			
8	Haloid Compounds.	Antimonious chloride	$SbCl_3$	228·5	2·67	53·39
9		,, oxychloride ..	$SbClO$			
10		Antimonic chloride	$SbCl_5$	299·5	2·34	
11		,, oxytrichloride ..	$SbCl_3O$			
12		,, sulpho-trichloride	$SbSCl_3$			
13		Antimonious bromide	$SbBr_3$			
14		,, iodide	SbI_3			
15		,, fluoride	SbF_3			
16		Antimonic ,, ...	SbF_5			
17	Sulphur Compounds	Antimonious sulphide	Sb_2S_3	340·0	4·6	71·77
18		Antimonic ,, ...	Sb_2S_5	404·0		60·4
19		Sulphantimonious acid ..	H_3SbS_3			
20		Sulphantimonic ,, ..	H_3SbS_4			

COMPOUND OF ANTIMONY AND HYDROGEN.

(1.) **Antimoniuretted** (or **Antimonetted**) **Hydrogen**; *Stibine; Antimonious hydride* ($SbH_3=125$).

Preparation.—By acting with dilute sulphuric acid either (*a.*) on zinc mixed with an antimonious salt, or (*β.*) on an alloy of zinc and antimony (*see* Nascent Hydrogen, p. 11).

$$SbCl_3 + 3H_2 = SbH_3 + 3HCl.$$

Antimonious chloride + Hydrogen = Antimonetted hydrogen + Hydrochloric acid.

Properties.—A colorless, combustible gas, forming, when burnt in a free supply of air, antimonious oxide and water ($2SbH_3+3O_2=Sb_2O_3+3H_2O$), but if the supply of air be limited, producing the metal and water, only the hydrogen in the latter case being oxidized ($4SbH_3+3O_2=Sb_4+6H_2O$). A piece of cold porcelain held in the flame of antimoniuretted hydrogen, becomes coated with a black film of the metal. The gas is decomposed into its elements when passed through a red hot tube.

If the gas be passed into a solution of argentic nitrate, a black precipitate of antimonious argentide ($SbAg_3$) is formed. (N.B.—AsH_3 precipitates metallic silver.)

$$3AgNO_3 + SbH_3 = 3HNO_3 + SbAg_3$$

Argentic nitrate + Antimoniuretted hydrogen = Nitric acid + Antimonious argentide.

From the above reaction the composition of the gas as SbH_3 may be inferred, exact determination being impossible, owing to its having never been obtained free from hydrogen. SbH_3 being its composition, its relationship to NH_3, to PH_3, and to AsH_3 becomes obvious. Moreover compounds of antimony with the alcohol-radicals, analogous to those formed by nitrogen, phosphorus and arsenic also exist, such as for example—trimethyl-(or ethyl or amyl) stibine $[Sb\,(CH_3)_3]$.

Compounds of Antimony and Oxygen.

2. Antimonious oxide (anhydride)	Sb_2O_3.
3. Metantimonious acid	$HSbO_2$.
4. Antimonious antimonic oxide ...	$Sb_2O_3,Sb_2O_5(=Sb_2O_4)$.
5. Antimonic oxide (anhydride) ...	Sb_2O_5.
6. Antimonic acid	$HSbO_3\ (= Sb_2O_5,H_2O)$.
7. Met-antimonic acid	$H_4Sb_2O_7\ (=Sb_2O_5,2H_2O)$.

(2.) Antimonious Oxide (or **Anhydride**); *Trioxide; Sesquioxide;* (Sb_2O_3). *Molecular volume,* $\boxed{}\boxed{}$.

Natural History.—Found native as *valentinite* (white antimony ore; Sp. gr. 5·56) and as *senarmontite.*

Preparation.—(1.) By the combustion of metallic antimony in a limited supply of air or oxygen ($2Sb_2+3O_2=2Sb_2O_3$).

(2.) By the action of heat on metantimonious acid ($2HSbO_2=H_2O+Sb_2O_3$).

(3.) By first digesting and afterwards heating the precipitate of the basic salt (formed when a solution of antimonious chloride is poured into water) in a solution of sodic carbonate :—

$2SbCl_3$	+	$3Na_2CO_3$	=	Sb_2O_3	+	$3CO_2$	+	$6NaCl$.
Antimonious chloride	+	Sodic carbonate	=	Antimonious oxide	+	Carbonic anhydride	+	Sodic chloride.

Properties.—A dimorphous body, crystallising (like As_2O_3) both in needles and in octahedra. It is yellow when hot, and white (or buff-colored) when cold. It is fusible, volatile, and combustible at a red heat, Sb_2O_4 constituting one of the products.

It is almost insoluble in water, and in dilute sulphuric acid. It is soluble both in hydrochloric acid ($SbCl_3$ being formed) and in tartaric acid (the tartrate being formed). By the action upon it of nitric acid, it is converted into antimonic anhydride (Sb_2O_5).

It is soluble in a boiling solution of hydric-potassic tartrate (cream of tartar), ($KHC_4H_4O_6$), forming the compound known as *tartar emetic* ($K,SbO,C_4H_4O_6$), which, unlike salts of antimony generally, is both soluble in, and undecomposed by, water.

By ignition in hydrogen or with carbon, the oxide is reduced to the metallic state ($Sb_2O_3+3C=2Sb+3CO$).

Antimonious oxide possesses both weak basic and weak acid properties. Thus, as a *weak base,* an insoluble antimonious sulphate ($Sb_2O_3,3SO_3$) is formed by the action of sulphuric acid upon it. As a *weak acid*, it is soluble in solutions of the fixed alkalies. Hence it is called *antimonious acid*, and its salts *antimonites* ($M'SbO_2$).

Uses.—As a substitute for white lead.

(3.) **Metantimonious Acid** ($HSbO_2$) is formed when antimonious chloride is poured into a cold solution of sodic carbonate. The antimonites are ill defined compounds. (*See above.*)

(4.) **Antimonious Antimonic Oxide**; *Diantimonic tetroxide* (Frankland); *Antimonoso-antimonic oxide* (Watts); ($Sb_2O_3,Sb_2O_5=Sb_2O_4$).

Natural History.—It is found in nature as cervantite (*antimony ochre*).

Preparation.—(*a.*) By the action of heat on antimonic oxide (Sb_2O_5), or (*β.*) by burning antimonious oxide (Sb_2O_3) in air.

$$(a.)\ 2Sb_2O_5 = 2Sb_2O_4 + O_2.$$

$$(\beta.)\ 2Sb_2O_3 + O_2 = 2Sb_2O_4.$$

Properties.—A grey, infusible, non-volatile powder, insoluble both in water and in acids.

Its constitution is doubtful:—

(*a.*) Some regard it as (Sb_2O_3,Sb_2O_5) because (1) when treated with tartaric acid, Sb_2O_3 passes into solution, and Sb_2O_5 remains undissolved; and (2) that when its solution in hydrochloric acid is dropped into water, Sb_2O_3 is precipitated, and Sb_2O_5 remains dissolved.

(*β.*) Others regard it as Sb_2O_4, because it is soluble in alkalies without decomposition. Thus it has weak acid characters, its salts, which have the general formula (M'_2O,Sb_2O_4), having been called *antimonites* and *hypo-antimonates*.

(5.) **Antimonic Oxide (or Anhydride)**; *Pentoxide* [formerly called *Antimonic acid*] (Sb_2O_5).

Preparation. — By heating the hydrates (*q. v.*) below redness to drive off combined water.

Properties.—Antimonic oxide is white when cold and yellow when hot. Sp. gr. 6·6. At 572° F.(300° C.) it is decomposed into Sb_2O_4 and free oxygen. It is insoluble both in water and in acids. It is soluble in, and forms definite compounds with, the alkalies. Fused with potassic carbonate, $KSbO_3$ is formed.

Hydrates (Acids) of Antimonic Oxide.

(7.) **Antimonic Acid**, or as it is sometimes called *met-antimonic acid* ($H_2O,Sb_2O_5=HSbO_3$), is formed when antimony is treated with nitric acid ($Sb_2+4HNO_3=N_2O_3+2HSbO_3+2NO_2+H_2O$). The acid is monobasic, forming normal and acid salts, commonly called *antimonates.*

(8.) **Met-antimonic Acid**, or as it is sometimes called *pyro-antimonic acid* ($2H_2O,Sb_2O_5=H_4Sb_2O_7$) is formed when antimonic chloride is treated with water. It forms both normal and acid salts, commonly called *metantimonates.*

Potassium antimonate ($KSbO_3$) is prepared by fusing a mixture of metallic antimony and nitre.

The *normal potassium metantimonate* ($K_4Sb_2O_7$) is prepared by fusing the antimonate with caustic potash, dissolving the fused mass in water, and crystallizing.

The *hydric-potassium metantimonate* ($K_2H_2Sb_2O_7,6H_2O$), prepared by acting on crystals of the normal salt with a small quantity of water, is used in the laboratory as a test reagent for sodium compounds, forming with them the insoluble salt (and the only insoluble sodium salt known) called *hydric-sodium metantimonate* ($Na_2H_2Sb_2O_7,6H_2O$). It should be remembered that the normal potassic antimonate ($K_4Sb_2O_7$), into which the acid antimonate rapidly passes, does not precipitate sodium salts.

COMPOUNDS OF ANTIMONY WITH CHLORINE, ETC.

9.	Antimonious chloride	$SbCl_3$.
10.	Antimonious oxychloride	$SbClO$.
11.	Antimonic chloride	$SbCl_5$.
12.	Antimonic oxytrichloride	$SbCl_3O$.
13.	Antimonic sulphotrichloride	$SbCl_3S$.
14.	Antimonious bromide	$SbBr_3$.
15.	,, iodide	SbI_3.
16.	,, fluoride	SbF_3.
17.	Antimonic fluoride	SbF_5.

(9, 10.) Antimonious Chloride; *Terchloride of antimony; Butter of antimony* ($SbCl_3$). *Molecular volume,* $\boxed{\quad\vert\quad}$.

Preparation.—(1.) By distilling corrosive sublimate with antimony or with antimonious sulphide :—

$$\begin{array}{ccccccccc} Sb_4 & + & 4HgCl_2 & = & 2SbCl_3 & + & Sb_2Hg_2 & + & Hg_2Cl_2. \\ \text{Antimony} & + & \text{Mercuric} & = & \text{Antimonious} & + & \text{Antimony} & + & \text{Mercurous} \\ & & \text{chloride} & & \text{chloride} & & \text{amalgam} & & \text{chloride.} \end{array}$$

(2.) By the action of hydrochloric acid on antimonious sulphide :—

$$\begin{array}{ccccccc} Sb_2S_3 & + & 6HCl & = & 3H_2S & + & 2SbCl_3. \\ \text{Antimonious} & + & \text{Hydrochloric} & = & \text{Sulphuretted} & + & \text{Antimonious} \\ \text{sulphide} & & \text{acid} & & \text{hydrogen} & & \text{chloride.} \end{array}$$

(3.) By the direct union of chlorine and the metal (or by the action of aqua regia on the metal):—

$$Sb_2+3Cl_2=2SbCl_3.$$

(4.) By passing chlorine over antimonious sulphide :—

$$2Sb_2S_3+9Cl_2=4SbCl_3+3S_2Cl_2.$$

(5.) By distilling sodic chloride with antimonious sulphate :—

$$Sb_23SO_4+6NaCl=2SbCl_3+3Na_2SO_4.$$

Properties.—A soft, crystallizable, deliquescent, corrosive solid. Sp. gr. 2·67. It is fusible at 161·6° F. (72° C.), and volatile at higher temperatures. It boils at 433° F. (223° C.). It is soluble in hydrochloric acid as well as in a *little water*, but is decomposed if an *excess of water* be employed, an insoluble oxychloride or "*powder of algaroth*" being formed ($3SbCl_3 + 3H_2O = SbCl_3,Sb_2O_3$ (or $3SbClO$) $+ 6HCl$). By the long-continued action of water the antimonious oxychloride becomes antimonious oxide [$2(SbCl_3,Sb_2O_3) + 3H_2O = 6HCl + 3Sb_2O_3$].

Uses.—For bronzing gun-barrels to prevent their rusting. As a caustic.

(11, 12, 13.) **Antimonic Chloride**; *Pentachloride of antimony* ($SbCl_5$).

Preparation.—By the action of an excess of chlorine on (α) metallic antimony ($Sb_2 + 5Cl_2 = 2SbCl_5$), or on (β) antimonious chloride ($SbCl_3 + Cl_2 = SbCl_5$).

Properties.—A colorless fuming liquid, having a suffocating odor. Mixed with a little water it forms white crystals of *antimonic oxy-trichloride* ($SbOCl_3$), but when treated with a quantity of water it forms *metantimonic acid* ($2SbCl_5 + 7H_2O = H_4Sb_2O_7 + 10HCl$). It absorbs sulphuretted hydrogen, forming the solid *antimonic chlorosulphide* (sulpho-trichloride) ($SbCl_3S$).

Use.—It is an active chlorinator, delivering up its chlorine with great ease.

The analogy of the compounds of phosphorus and of antimony with chlorine and oxygen may be noted here. Thus, $SbCl_3$ and $SbCl_5$ correspond to PCl_3 and PCl_5, whilst the chlorosulphide of antimony ($SbCl_3S$) corresponds to the chlorosulphide of phosphorus (PCl_3S).

Compounds of Antimony and Sulphur, etc.

18.	Antimonious sulphide	Sb_2S_3.
19.	Antimonic sulphide	Sb_2S_5.
20.	Sulph-antimonious acid	H_3SbS_3.

(18.) **Antimonious Sulphide** (Sb_2S_3); *Tersulphide* or *Sesquisulphide of antimony*; *Sulphantimonious anhydride* (Frankland); *Kermes mineral* (*i.e.*, from its color being like the cochineal insect. The true Kermes mineral, however, is a mixture of antimonious sulphide and oxide in uncertain proportions).

Natural History.—It occurs as stibnite (grey antimony ore), and in combination with numerous other sulphides.

Preparation.—(1.) By heating together (α) antimony and sulphur, or (β) antimonious oxide and sulphur—

(α.) $Sb_4 + 3S_2 = 2Sb_2S_3$. (β.) $2Sb_2O_3 + 9S = 2Sb_2S_3 + 3SO_2$.

(2.) By passing sulphuretted hydrogen through a solution of tartar emetic or of antimonious chloride ($2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl$).

Properties.—The native compound is grey, brittle, crystalline (four-sided prisms), and fusible. The sulphide, as precipitated by H_2S, is orange-red (*antimony vermilion*), but becomes grey and crystalline on the application of heat.

In closed vessels it may be distilled unchanged, but when heated in open vessels it forms an *oxy-sulphide* ($Sb_2O_3,2Sb_2S_3 = 3Sb_2S''_2O$), which when fused, constitutes "*glass of antimony.*" "Red antimony ore" is a native oxy-sulphide. It is decomposed by hydrochloric acid ($Sb_2S_3+6HCl = 3H_2S+2SbCl_3$).

(20.) **Sulphantimonious Acid; Sulphantimonites.**—Antimonious sulphide is soluble in a solution of an alkaline sulphide or of an alkaline hydrate, soluble salts known as *antimonites* and *sulphantimonites* being formed :—

Sb_2S_3	+	$6KHO$	=	K_3SbS_3	+	K_3SbO_3	+	H_2O.
Antimonious sulphide	+	Potash	=	Potassic sulph-antimonite	+	Potassic antimonite	+	Water.

The solution, when concentrated, deposits a red powder, consisting of a mixture of antimonious oxide and antimonious sulphide in varying proportions (*Kermes mineral*). If an acid be added to a solution of this compound, Sb_2S_3 is precipitated.

The sulphantimonites are found native as lead, silver, copper, and iron salts, *e.g.*, $AgSbS_3$; $Pb(SbS_3)_2$.

(19.) **Antimonic Sulphide**; *Pentasulphide of antimony; Sulphantimonic anhydride; Sulphur auratum* (Sb_2S_5).

Preparation.—(1.) By passing sulphuretted hydrogen through a solution of antimonic chloride ($2SbCl_5+5H_2S = Sb_2S_5+10HCl$).

(2.) By the action of an acid on a sulphantimonate, *e.g.*, on *sodium sulphantimonate*, Na_3SbS_4. (This salt is prepared by crystallizing the solution formed when antimonious sulphide, sodium carbonate, lime and sulphur are boiled together.)

Properties.—An orange yellow body, decomposed by heat, Sb_2S_3 and S being formed, and also by boiling in hydrochloric acid ($Sb_2S_5+6HCl=2SbCl_3+3H_2S+S_2$).

(20.) **Sulphantimonic Acid** (H_3SbS_4 ?); **Sulphantimonates.**—When antimonic sulphide (Sb_2S_5) is acted on either with an alkaline sulphide or an alkaline hydrate, a sulphantimonate is formed :—

Sb_2S_5	+	$3K_2S$	=	$2K_3SbS_4$
Antimonic sulphide	+	Potassic sulphide	=	Potassic sulph-antimonate.

The sodium sulphantimonate (Na_3SbS_4) is known as "*Schlippe's salt.*"

REACTIONS OF THE COMPOUNDS OF ANTIMONY.

[NOTE.—Antimony compounds (excepting tartar emetic) are for the most part insoluble in water.]

1. *Sulphuretted hydrogen.*—An orange (or yellowish-red) ppt. in a HCl solution of Sb_2S_3. Precipitate is soluble in ammonium sulphide, in caustic alkalies, and in concentrated HCl. Insoluble in ammonium carbonate (*See* Arsenic).

2. *Caustic alkalies* (potash or soda) *and their carbonates.* A white ppt. of hydrated oxide, Sb_2O_3,H_2O. Soluble in tartaric acid.

3. A piece of zinc placed in an hydrochloric acid solution of a compound of antimony contained in a platinum dish precipitates the metal as a black deposit on the platinum.

4. In the presence of nascent hydrogen, antimony compounds yield SbH_3 (which see). If the gas be heated whilst passing through a glass tube, the metal will be deposited on the tube. This film will be found to be insoluble in a solution of sodium hypochlorite. (*See* Arsenic.)

5. Heated on charcoal with sodium carbonate, antimony compounds give a white incrustation of Sb_2O_3, but no garlic odor.

ARSENICUM (As = 75).

Atomic weight, 75. *Molecular weight*, 300 (*See p.* 39.) *Molecular volume*, ☐☐. *Specific gravity*, 5·7 *to* 5·9. *Specific heat*, 0·0814. *Atomicity, triad, as in arsenious compounds* (*e.g.*, $AsCl_3$), *and pentad, as in arsenic compounds* (*e.g.*, As_2O_5).

History.—Arsenic has been known from a very early date. The word ἀρσενικον was employed as early as the fourth century by Theophrastus. The metal was first prepared by Brandt, in 1733.

Natural History.—It is found native both in a free state and alloyed with other metals, such as Co, Fe, Ni, etc. It sometimes occurs as a *sulphide* (*realgar*, As_2S_2, and *orpiment*, As_2S_3), but is more frequently found in combination with metals as an *arsenide*, as *e.g.*, *kupfernickel* (NiAs and $NiAs_2$), *tin-white cobalt* ($CoAs_2$). Frequently it is found as an arsenio-sulphide, as *mispickel* or arsenical pyrites ($FeS_2,FeAs_2$), or as *cobalt glance* ($CoS_2,CoAs_2$), or as *nickel glance* ($NiS_2,NiAs_2$), etc. It is found in some mineral waters, in soils, in commercial zinc, in coal smoke (from pyrites), etc. It is invariably present in commercial sulphuric and hydrochloric acids.

Preparation.—By the reduction of arsenious anhydride with charcoal. The metal, being volatile, sublimes ($As_2O_3 + 3C = As_2 + 3CO$).

Properties.—(*a.*) *Physical.* Its molecular weight, deduced from its vapor density, is 300; in other words, the vapor density (150) of arsenicum, is twice that of its atomic weight (75), instead of, as in the case of most of the other elements, being the same as its atomic weight. The molecule, therefore, is assumed to be (like that of phosphorus) tetratomic (As^{iv}), and its molecular weight, $75 \times 4 = 300$. At very high temperatures, however, partial dissociation occurs, the molecule being between As_2 and As_4.

Arsenicum occurs both in an amorphous form (Sp. gr. 5·71) and as crystals (Sp. gr. 5·9), having a brilliantly metallic steel-grey lustre. The amorphous variety changes to the crystalline when heated to 680° F. (360° C.). When heated under ordinary pressure to 356° F. (180° C.) arsenicum volatilises without fusing, but the metal may be fused by heating it in a sealed tube, so that it may be subjected to the pressure of its own vapor. It is a conductor of electricity. The metal is not a poison until it becomes oxidised.

(β.) *Chemical.* When the dry metal is exposed to dry air it undergoes no change, but the powdered metal in the presence of moisture slowly oxidises, forming " fly-powder," probably a mixture of metallic arsenic and As_2O_3. Heated to 160° F. (71° C.) in air or oxygen, it gives off condensible, colorless, garlic-smelling fumes of As_2O_3. At a red heat, the metal burns with a white flame. It may be preserved unchanged in pure water. The powdered metal fires spontaneously when thrown into chlorine, its union, when heated in contact with bromine, iodine, and sulphur, being also energetic. Nitric acid converts it into arsenic acid. Hydrochloric acid has no action upon it, unless it be mixed with potassic chlorate, when arsenic acid is formed. It is soluble in a solution of bleaching powder (calcium hypochlorite).

Some chemists regard arsenicum as a non-metal. In support of this view they urge its many analogies to phosphorus and nitrogen. Like the former, it burns spontaneously when placed in chlorine, and combines readily with sulphur and with the metals. Moreover, it is capable of existing in various allotropic modifications, each possessing a different specific gravity. Others regard it as a *metal,* because of its high metallic lustre, its power of conducting electricity, its insolubility in common solvents, and the ease with which it forms alloys, the properties of the metals with which it is associated being more or less affected by admixture.

Uses.—For fly-powder. In the manufacture of lead shot, a small quantity of arsenic being added to the lead in order to increase its hardness, and to facilitate the lead assuming a globular form.

Compounds of Arsenic ($As = 75$).

		COMPOUNDS.	Formulæ (General).	Molecular Weight.	Specific Gravity.	As per cent.
1		Arseniuretted hydrogen	AsH_3	78·0	2·695	96·15
2	Oxides.	Arsenious anhydride (oxide) ..	As'''_2O_3	198·0	3·7	75·76
3		,, acid	H_3AsO_3			
4		Arsenic anhydride (oxide) ..	As_2O_5	230		65·22
5		,, acid	H_3AsO_4	162		
6	Sulphides.	Arsenious disulphide (realgar)	As_2S_2	214·0	3·5	70·09
7		,, sulphide (orpiment)	As_2S_3	246·0	3·5	60·97
8		Sulpharsenious acid..	H_3AsS_3			
9		Arsenic sulphide	As_2S_5	310·0		48·38
10		Sulpharsenic acid	H_3AsS_4			
11		Arsenious chloride	$AsCl_3$	181·5	2·205	
12		,, bromide	$AsBr_3$		3·66	
13		,, iodide	AsI_3	456·0	4·39	
14		,, trifluoride	AsF_3			
15		,, pentafluoride	AsF_5			

COMPOUND OF ARSENIC AND HYDROGEN.

Arseniuretted hydrogen ... ... AsH_3.

(1.) Arseniuretted (or Arsenetted) Hydrogen (AsH_3).—*Arsenious hydride; arsine; trihydride of arsenic.*

History.—Discovered by Scheele (1755).

Preparation.—(1.) By acting with dilute sulphuric acid, either (α) on a mixture of zinc and arsenious acid, or (β) on an alloy of zinc and arsenicum (*zinc arsenide*). (Action of nascent hydrogen, *see* page 11)—

(α.) $As_2O_3 + 6Zn + 6H_2SO_4 = 2AsH_3 + 6ZnSO_4 + 3H_2O$.

(β.) $As_2Zn_3 + 3H_2SO_4 = 3ZnSO_4 + 2AsH_3$.

(2.) By boiling a solution of caustic potash containing arsenious acid with pieces of metallic zinc or aluminium (*Fleitmann's test*). This reaction serves to distinguish arsenic from antimony compounds.

Properties.—(α.) *Sensible and Physical.* A colorless, garlic-smelling, intensely poisonous gas. Sp. gr. 2·695. It is slightly soluble in water. It liquifies at —22° F. (—30° C.). It has not as yet been solidified. It is decomposed at a low red heat into its constituents.

(β.) *Chemical.* Its reaction is neither acid nor alkaline. It burns with a bluish-white flame, forming water and arsenious anhydride if the supply of air be free ($2AsH_3 + 3O_2 = As_2O_3 + 3H_2O$), or water and the metal if the supply be limited ($4AsH_3 + 3O_2 = As_4 + 6H_2O$). The flame deposits metallic arsenic (which, unlike the antimony film, is soluble in a solution of sodium hypochlorite) on bodies placed within it, and arsenious anhydride on bodies placed above it. If the gas be passed through a glass tube heated at one spot with a Bunsen burner, a mirror of the metal is formed in front of the heated portion of the tube (*Marsh's test*). If this metallic deposit be heated whilst a current of air is passed through the tube, octahedral crystals of arsenious anhydride are formed. The gas is decomposed by chlorine, hydrochloric acid and a solid hydride (As_4H_2 ?) being formed. The gas is absorbed by *nitric acid*, arsenic acid being produced; also by *cupric sulphate*, an arsenide of copper being precipitated ($2AsH_3 + 3CuSO_4 = 3H_2SO_4 + As_2Cu_3$); also by *argentic nitrate*, arsenious and nitric acids being formed and the silver precipitated ($AsH_3 + 6AgNO_3 + 3H_2O = 6HNO_3 + H_3AsO_3 + 3Ag_2$) (*Hoffmann's test*). The gas is also absorbed by a solution of corrosive sublimate, by oil of turpentine, etc. Chemically, arseniuretted hydrogen (AsH_3) is closely related to ammonia (NH_3) and to phosphoretted hydrogen (PH_3), all three gases being inflammable, possessing a peculiar smell, being decomposed by heat, and formed by the action of nascent hydrogen on the corresponding oxygen compounds (*viz.*, N_2O_3; P_2O_3; Cu_2O_3).

Arseniuretted hydrogen is a virulent poison.

A *solid hydride* (H_4As_2 (Soubeiran) or As_4H_2 (Wiederhold),) is said to be formed when a plate of arsenicum is used as the negative pole in the electrolysis of water, and when sodium arsenide is decomposed by the action of water.

COMPOUNDS OF ARSENIC AND OXYGEN, ETC.

2.	Arsenious anhydride	As_2O_3.
3.	„ acid	H_3AsO_3.
4.	Arsenic anhydride	As_2O_5.
5.	„ acid	H_3AsO_4.

(2, 3.) **Arsenious Anhydride**; *Arsenious acid; Arsenic trioxide; White arsenic; Arsenic* (As_2O_3).—**Arsenious Acid** ($H_3AsO_3 = As_2O_3, 3H_2O$). (The acid is only known in solution.)

Natural History.—Arsenic is found native as arsenite, or "arsenic bloom."

Preparation.—Either (1) by roasting arsenical ores in a current of air, or (2) by heating arsenicum in air.

Properties.—(*a.*) *Physical.* Arsenic exists in two forms:—(1.) A *vitreous form* (specific gravity 3·738). This variety is transparent and colorless when first prepared, but becomes opaque, yellowish-white, and somewhat like porcelain, after exposure to air. (2.) A *crystalline form* (specific gravity, 3·695). This variety is formed when arsenic is carefully sublimed in small quantities (rhombic crystals), or is crystallized from a hydrochloric acid solution (octahedral crystals.)

Arsenic is very nearly, if not entirely, destitute both of taste and smell. The opaque variety has a lower specific gravity than the transparent. Heat converts the opaque form into the vitreous, whilst mere grinding in a mortar converts the vitreous into the opaque. Heated to 380° F. (193° C.), arsenic softens and sublimes without fusing, yielding transparent octahedral crystals on warmed surfaces. A somewhat characteristic behaviour of arsenic is the white layer it forms when thrown in a state of powder upon the surface of water, the particles of arsenic repelling the water and collecting round the air bubbles.

The solubility of arsenic in water is a question of considerable medico-legal importance. The following are the chief circumstances that serve to modify the solvent action of water on the acid:—

1. The peculiar modification of acid used.
2. Its admixture or contamination with organic matter. It is said that the presence of greasy matter, such as bacon, reduces the solubility of arsenious acid to one-twentieth its usual solubility. If this be the fact, it affords a partial explanation why its action on the human body should seem at times to be suspended.—(Dr. Blondlot, "Medical Times and Gazette," Feb. 11, 1860.)
3. The length of time the water has acted.
4. The temperature of the water employed.
5. If boiled, the length of time the boiling has been continued.
6. The time that has elapsed between boiling and the examination.

We state a few results illustrating the solubility of the acid under different conditions, in a tabular form:—

Solubility of Arsenious Acid.

	Transparent form.	Opaque form.	Fresh crystalline acid.
1000 grains of cold distilled water, after standing for 24 hours, dissolved	1·74 grains.	1·16 grains.	2·0 grains.
1000 grains of boiling water poured on the acid, and allowed to stand for 24 hours, dissolved	10·12 ,,	5·4 ,,	15·0 ,,
1000 grains of water boiled for one hour, (the quantity being rendered uniform by the addition of boiling water from time to time) and filtered immediately, dissolved	64·5 ,,	76·5 ,,	87·0 ,,

(β.) *Physiological.*—Arsenic is an active poison. *Ferric hydrate* ($Fe_2H_6O_6$) is an antidote frequently administered, which, to be of use, must be given in large doses, and be *freshly prepared* by adding calcined magnesia to a solution of iron chloride or sulphate ($Fe_2Cl_6 + 3MgO + 3H_2O = Fe_2H_6O_6 + 3MgCl_2$). By the use of this antidote, the arsenious acid will be oxidized to arsenic acid, the arsenic acid forming with another portion of the $Fe_2H_6O_6$ a basic ferric arsenate, which is insoluble either in water or in dilute acids.

(γ.) *Chemical.*—A solution of arsenious acid (*i. e.*, arsenious anhydride dissolved in water), has a feebly acid reaction. It readily combines with bases, the salts being called *arsenites*, but it does not neutralize the alkalies, nor does it decompose alkaline carbonates unless heated with them. The arsenites generally are easily decomposed by a stronger acid. The arsenites of the alkalies are soluble in water and very poisonous. The other arsenites are almost insoluble; hence the action of lime and magnesia as antidotes. Most of the arsenites are decomposed by heat, whilst all, when heated with a reducing agent, evolve the metal in a vaporous form. The copper arsenite, or Scheele's green, and the silver arsenite are the two most important salts of arsenious acid.

Arsenious acid is readily soluble in solutions of the fixed caustic alkalies, but is not very soluble in ammonia. It is very slightly soluble in sulphuric acid. It is freely soluble in hot nitric acid, the arsenious being changed to arsenic acid. It is also soluble in hydrochloric and in some vegetable acids, in alcohol (1 in 2000 of alcohol of specific gravity 0·802), and in chloroform (1 in 200,000), but is insoluble in absolute ether. When chlorine is passed through a solution of arsenious acid, arsenic acid is formed.

(*See* Arsenites, p. 333.)

Uses.—In the manufacture of glass. The solutions of the arsenites of potash and soda are used as sheep dipping compositions. An arsenical soap (camphor, soap, and arsenite of potash) is used as a preservative for the skins of animals. Arsenite of soda is used as a means for preventing the incrustation of boilers. Arsenite of copper (*Scheele's green*) is used as a pigment for paper-hangings, feathers, muslins, etc. Arsenic and arsenite of potash (Fowler's solution) are used in medicine.

(4, 5.) **Arsenic Anhydride** (As_2O_5).—**Arsenic Acid,** $H_3AsO_4 = As_2O_5,3H_2O$.

Preparation.—(1.) (*Anhydride.*) By the action of heat on solid arsenic acid ($2H_3AsO_4 = As_2O_5+3H_2O$).

(2.) (*Acid.*)—(α.) By oxidizing arsenious anhydride with nitric acid or aqua regia ($As_2O_3+2HNO_3+2H_2O=N_2O_3+2H_3AsO_4$).

(β.) By passing chlorine through an aqueous solution of arsenious oxide.

Properties. — *Physical.* The anhydride is a white deliquescent substance, soluble in water forming H_3AsO_4. When heated it undergoes decomposition ($A_2O_5=As_2O_3+O_2$).

The acid on cooling deposits crystals having the composition $As_2O_5,3H_2O + aq$. At 212° F. (100° C.) these crystals melt, and lose their water of crystallization, becoming $As_2O_5,3H_2O=2H_3AsO_4$ (ortho-arsenic acid). Heated to 320° F. (160° C.) $As_2O_5,2H_2O$ ($=H_4As_2O_7$, pyro-arsenic acid) is formed. At 392° F. (200° C.), it becomes As_2O_5,H_2O ($=HAsO_3$ met-arsenic acid), and at 500° F. (260° C.), arsenic anhydride only (As_2O_5) is left.

Chemical.—The anhydride is decomposed by gaseous hydrochloric acid ($As_2O_5+10HCl=2AsCl_3+2Cl_2+5H_2O$).

Arsenic Acid is tribasic (H_3AsO_4). It forms salts called *arsenates*, which closely resemble, and are isomorphous with, the tribasic phosphates. (*See* Arsenates, p. 331.)

When heated with strong hydrochloric acid, arsenic acid forms the volatile $AsCl_3$ ($H_3AsO_4 + 5HCl = AsCl_3 + Cl_2 + 4H_2O$). It is reduced to arsenious acid by sulphurous acid ($H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4$).

Uses.—Arsenic acid is used in the preparation of magenta by its action on aniline. *Arsenate of soda* is used by the calico-printers as a dung substitute.

Compounds of Arsenic and Sulphur.

6.	Arsenious disulphide (realgar)	As_2S_2.
7.	Arsenious sulphide (sulpharsenious anhydride; orpiment)	As_2S_3.
8.	Sulph-arsenious acid	H_3AsS_3.
9.	Arsenic sulphide (sulph-arsenic anhydride) ...	As_2S_5.
10.	Sulph-arsenic acid	H_3AsS_4

(6.) **Arsenious Disulphide**; *Realgar.* (As_2S_2.) This sulphide is found native in ruby red crystals.

Preparation.—(1.) By heating sulphur with arsenious anhydride ($2As_2O_3 + S_7 = 2As_2S_2 + 3SO_2$).

(2.) By heating ferric sulphide with arsenical pyrites ($(As_2S_2,2FeS) + 2FeS_2 = As_2S_2 + 6FeS$).

Properties.—A red, transparent, fusible, volatile, and crystalline solid (Sp. gr. 3·5), burning with a blue flame, SO_2 and As_2O_3 forming the products of combustion. It is insoluble in water and in hydrochloric acid. It is soluble in nitric acid (forming arsenic and sulphuric acids), also in aqua regia and in potassic disulphide. It is decomposed by the fixed alkalies, leaving, as a precipitate, a brown arsenical subsulphide. It is used in the manufacture of fireworks.

(7, 8.) **Arsenious Sulphide** (As_2S_3); *Arsenious sesquisulphide; Ter-sulphide of Arsenic; Sulph-arsenious anhydride; Orpiment; Sulph-arsenious acid* (H_3AsS_3).

Natural History.—Found native both in a crystalline and massive form as orpiment.

Preparation.—(*Anhydride.*) (1.) By passing sulphuretted hydrogen through a solution of arsenious acid acidulated with hydrochloric acid :—

$3H_2S$	+	$2AsCl_3$	=	$6HCl$	+	As_2S_3
Sulphuretted hydrogen	+	Arsenious chloride	=	Hydrochloric acid.	+	Arsenious sulphide.

(2.) By subliming a mixture of sulphur and arsenious anhydride :—

$9S$	+	$2As_2O_3$	=	$2As_2S_3$	+	$3SO_2$
Sulphur	+	Arsenious anhydride	=	Arsenious sulphide	+	Sulphurous anhydride.

Properties.—A yellow, crystalline, fusible, and volatile substance (specific gravity, 3·5), insoluble in water and in dilute acids. It is decomposed by nitric acid and by aqua regia. It burns in air, but may be sublimed in closed vessels. It is a feeble sulphur acid. It is soluble in ammonic carbonate (in which the corresponding tin and antimony sulphides are insoluble), and also in the alkalies, an alkaline arsenite and *sulpharsenite* being formed :—

$12KHO$	+	$2As_2S_3$	=	$3K_2S,As_2S_3$	+	$3K_2O,As_2O_3$	+	$6H_2O.$
Potassic hydrate	+	Arsenious sesquisulphide	=	Potassic sulph-arsenite	+	Potassic arsenite.	+	Water.

On adding an acid to this solution, an arsenious sulphide (As_2S_3) is reprecipitated. (*Confer* Sulpharsenites, p. 334.)

Uses.—It is used as a pigment (King's yellow). The ammoniacal solution is used for dyeing, the colour being deposited as the ammonia evaporates.

(9, 10.) **Arsenic Sulphide** (As_2S_5); *Sulpharsenic anhydride; Diarsenic pentasulphide; Sulpharsenic acid* (H_3AsS_4).

Preparation.—(1.) (*Anhydride.*) By fusing a mixture of sulphur and orpiment.

(2.) (*a*.) By passing sulphuretted hydrogen through a solution of sodic arsenate, a solution of *sulph-arsenate of sodium* is formed :—

Na_3AsO_4	+	$4H_2S$	=	$4H_2O$	+	Na_3AsS_4.
Sodic arsenate	+	Sulphuretted hydrogen	=	Water	+	Sodic sulpharsenate.

(*β*.) When hydrochloric acid is added to this solution, *arsenic sulphide* is precipitated :—

$2Na_3AsS_4$	+	$6HCl$	=	$6NaCl$	+	$3H_2S$	+	As_2S_5.
Sodic sulpharsenate	+	Hydrochloric acid	=	Sodic chloride	+	Sulphuretted hydrogen	+	Arsenic sulphide.

Properties.—A yellow, volatile, fusible substance, solidifying after fusion to an orange-colored glass. *Sulpharsenic acid* (H_3AsS_4) is one of the most powerful of the sulphur acids. It forms salts analogous to the phosphates, called *sulph-arsenates* ($M'AsS_3$, *meta-sulpharsenate ;* $M_4As_2S_7$, *pyro-sulpharsenate ;* $M_3As'S_4$, *ortho-sulpharsenate*).

[*Confer* Sulph-arsenates.]

(8.) **Arsenious Chloride** ; *Terchloride of arsenic* ($AsCl_3$). *Atomic Weight,* 181·5. *Molecular volume,* .

Constitution.—Half a volume of arsenic vapor + 3 volumes of Cl = 2 volumes of $AsCl_3$.

Preparation.—(1.) By burning the metal in chlorine.

(2.) By passing dry chlorine over heated arsenious anhydride.

(3.) By distilling together (*a*) arsenious anhydride and mercuric chloride ; or (*β*.) arsenious anhydride, sodic chloride, and sulphuric acid ; or (*γ*) arsenious anhydride and hydrochloric acid :—

(*a*.) $As_2O_3+6HgCl_2 = 3Hg_2Cl_2+2AsCl_3$.

(*β*.) $As_2O_3+6NaCl+6H_2SO_4 = 6NaHSO_4+3H_2O+2AsCl_3$.

(*γ*.) $As_2O_3+6HCl = 3H_2O+2AsCl_3$.

Properties.—A heavy (specific gravity 2·2), pungent, oily, volatile, and fuming liquid, boiling at 269·6° F. (132° C.), and remaining fluid at —20·2° F. (—29° C.). It is decomposed when treated with a large quantity of water ($2AsCl_3 + 3H_2O = As_2O_3 + 6HCl$), but if a little water only be added to it, crystals of the oxychloride are formed ($AsClO$). It absorbs ammonia, forming a crystalline compound ($AsCl_3$, $2NH_3$).

(12, 13.) **Arsenious Bromide** ($AsBr_3$) and **Arsenious Iodide** (AsI_3) are prepared by adding As_2O_3 to a solution of bromine or of iodine in bisulphide of carbon. They are both solid bodies. The bromide is colorless, and the iodide of an orange color. $AsBr_3$ fuses at about 77° F. (25° C.). $AsBr_3$ is decomposed on the addition of water, in which respect it differs from AsI_3.

(14, 15.) **Arsenious Fluoride** (AsF_3) is prepared by distilling arsenious anhydride with fluor spar and sulphuric acid. A colorless liquid. Specific gravity 2·7. Boils at 145·4° F. (63° C.). Decomposed by water.

Arsenic pentafluoride, AsF_5, is only known in combination, as in the compound (AsF_5,KF).

REACTIONS OF ARSENIC COMPOUNDS.

(For details *see* MANUAL OF TOXICOLOGY.)

1. *Reactions of Compounds of Arsenic.*

(1.) *Sulphuretted hydrogen* :—A yellow precipitate (in HCl solution) of As_2S_3, soluble both in ammonium sulphide and in ammonium carbonate (*see* Antimony); soluble also in the caustic alkalies, etc.

(2.) Solutions acidulated with HCl and warmed with copper foil, yield a grey deposit of metallic arsenic on the copper (Reinsch's test).

(3.) This deposit (2), on being heated in the presence of air, gives a white sublimate of As_2O_3.

(4.) In the presence of nascent hydrogen, arsenious compounds yield AsH_3 (*q. v.*) (Marsh's test). If this gas be heated during its passage through a glass tube, the metal is condensed, as a brilliant mirror-like deposit, just *beyond* the heated portion. This film is soluble in a solution of sodium hypochlorite (*see* Antimony).

(5.) Heated on charcoal with Na_2CO_3, arsenic compounds evolve a garlic odor.

(6.) Compounds of arsenic yield a black sublimate of the metal when heated in a tube with a mixture of potassium cyanide and sodium carbonate.

2. *Reactions of Arsenates in Solution* (alkaline arsenates only being soluble).

(1.) *Silver nitrate* in neutral solutions :—A brown precipitate (Ag_3AsO_4), soluble in excess both of nitric acid and of ammonia.

(2.) *Ammonium molybdate* :—A yellow precipitate on boiling.

(3.) A mixture of *magnesium sulphate, ammonium chloride, and ammonia* :—A white precipitate of ammonium magnesic arsenate ($MgNH_4,AsO_4,6H_2O$).

(4.) *Sulphuretted hydrogen*, in acid solutions, slowly reduces arsenic to arsenious acid, and then throws down As_2S_3 (*see above*). [This action is assisted by heat.]

3. *Reactions of Arsenites in Solution.*

(1.) *Sulphuretted hydrogen*:—A yellow precipitate of As_2S_3 in an acid (HCl) solution.

(2.) *Silver nitrate* :—A yellow precipitate (Ag_3AsO_3), soluble in excess both of nitric acid and of ammonia.

VANADIUM (V).

Atomic weight, 51·3. *Molecular weight*, 205·2 (?) *Specific gravity*, 5·5. *Atomicity, pentad and triad.*

History.—Discovered by Del Rio (1801). Re-discovered by Sefström (1830). First isolated by Roscoe.

Natural History.—Occurs in certain lead (vanadinite) and iron ores; also in mottramite, a double vanadate of lead and copper; and in volborthite and pucherite (copper and bismuth vanadates). Found in the Bessemer slag of the Creusot iron works.

Preparation.—By heating vanadous chloride (VCl_3) in a current of dry hydrogen, air and moisture being excluded.

Properties.—A silvery metal, oxidizing slowly in air, and not decomposing water at ordinary temperatures. Specific gravity, 5·5. Infusible at a red heat. Can be heated to redness in vacuo without melting. Burns in air or oxygen, forming V_2O_5. At a red heat, the metal combines with nitrogen. It is soluble in dilute nitric acid (forming a blue solution), and in strong sulphuric acid. Insoluble in hydrochloric acid. The metal forms a vanadate when fused with the caustic alkalies, hydrogen being evolved.

COMPOUNDS OF VANADIUM.

(1.)	Hypovanadous oxide	V_2O_2
(2.)	Vanadous oxide	V_2O_3
(3.)	Hypovanadic oxide	V_2O_4
(4.)	Vanadic oxide (anhydride)	V_2O_5
(5.)	Metavanadic acid	HVO_3
(6.)	Vanadic acid	H_3VO_4
(7.)	Pyrovanadic acid	$H_4V_2O_7$
(8.)	Hypovanadous chloride	VCl_2
(9.)	Vanadous chloride	VCl_3
(10.)	Vanadic chloride	VCl_4

(4.) **Vanadic Anhydride** (V_2O_5) forms with water the tribasic acid (H_3VO_4). The anhydride is a reddish powder, soluble both in acids and in alkalies, and slightly soluble in water. It may be prepared by heating ammonium vanadate.

Vanadic acid forms salts, called vanadates, isomorphous with phosphates (see page 332). The acids of these salts, however, have not been prepared in a free state.

Ammonium vanadate is obtained by fusing the ore with potassic nitrate, extracting the potassic vanadate with water, and precipitating the vanadium in the clear filtrate as barium vanadate with $BaCl_2$. The barium salt is then boiled with dilute sulphuric acid, the $BaSO_4$ filtered off, the acid solution neutralized with ammonia, and lumps of solid ammonic chloride added. The ammonium vanadate being insoluble in a concentrated solution of NH_4Cl, will be precipitated in the form of small crystals.

NIOBIUM (Nb = 94). TANTALUM (Ta = 182).

Atomicity, triad and pentad.

Natural History.—Very rare metals. They occur together as tantalates and niobates in the minerals tantalite, columbite, etc.

Roscoe obtained pure niobium, having a Sp. gr. of 4·06, by reducing the chloride in hydrogen. Pure tantalum has not been prepared.

These metals form chlorides, oxides, etc. :—

Chlorides, etc., $NbCl_5$; $NbOCl_3$; NbF_5.
Oxides Nb_2O_2 ; Nb_2O_4 ; Nb_2O_5 (*anhydride*).

Tantalum forms similar compounds to those of niobium, except that corresponding to the oxide Nb_2O_2.

Tantalates (salts of the hydrate of Ta_2O_5), give a yellow precipitate with potassium ferrocyanide, and impart no color to a borax bead.

Niobates (salts of the hydrate of Nb_2O_5), give a brown precipitate with potassium ferrocyanide, and render a borax bead of a brown color.

GOLD (*Aurum*) (Au).

Atomic weight, 196·7. *Molecular weight* (*probable*), 393·4. *Specific gravity*, 19·4. *Fuses at from* 2012° F. *to* 2192° F. (1100° C. *to* 1200° C.). *Specific heat* 0·0324. *Atomicity, monad* (′) *in aurous compounds* ($AuCl$; Au_2O), *and triad* (‴) *in auric compounds* ($AuCl_3$; Au_2O_3).

History.—Known to the ancients (⊙ Sol).

Natural History.—Gold is always found in the metallic state. It occurs as cubes and octahedra (gold dust) in the alluvial sand of certain rivers, and also in masses (nuggets) or disseminated in quartz veins in certain volcanic rocks. It is, moreover, always found alloyed with silver (the alloy being called *electrum* if the silver exceeds 36 per cent.), frequently with copper, and sometimes with osmium, iridium, antimony and tellurium.

Extraction.—(1.) *Process of washing.* This consists in treating the well-powdered ore with water, whereby the sand is mechanically washed away from the gold, owing to the different specific gravity of the sand and the metal.

(2.) *Process of amalgamation.* This consists in dissolving out the gold in mercury from the *débris* with which it is associated, the quicksilver being afterwards separated from the gold by the distillation of the amalgam formed.

(3.) Sometimes the gold ore is fused with a mixture of metallic lead, lime, and oxide of iron. The lead in a state of fusion dissolves the gold, the liquid alloy sinking to the bottom of the slag. The gold is afterwards separated from the lead by cupellation (*see* Lead).

Preparation of pure gold.—Dissolve the gold in aqua regia (one part of HNO_3 and four parts of HCl), and add to the solution ferrous sulphate or other reducing agent. The ferrous sulphate will become oxidised to ferric sulphate, whilst the gold will be precipitated. The precipitate will appear brown by reflected, and purple by transmitted light ($6FeSO_4+2AuCl_3=2(Fe_23SO_4)+Fe_2Cl_6+Au_2$).

On boiling this precipitate with hydrochloric acid, certain impurities, such as iron, will be removed. The pure precipitated metal is then fused under a mixture of borax and nitre.

Properties.—(*a.*) *Physical.* A soft, heavy, yellow metal, possessing great lustre (Sp. gr. 19·4). It is the most ductile and malleable metal known, and also one of the most perfect conductors of heat and electricity. It fuses at 2258·6° F. (1237° C.), shrinking greatly in bulk as it solidifies. It is volatile at the heat of the oxy-hydrogen jet, giving off a purple vapor. A very fine leaf of gold is transparent to the green rays of light.

(*β.*) *Chemical.* Gold is unaffected at any temperature either by air or moisture. Sulphuretted hydrogen is without action upon it. It is soluble in chlorine or bromine water, in aqua regia, or in any mixture which, like aqua regia, liberates chlorine (forming $AuCl_3$) ; but it is insoluble either in any simple acid (except selenic acid) or in solutions of the alkalies. It combines readily with phosphorus by heat, and with the haloid elements in the cold. Most metals, and reducing agents generally, precipitate it from its solutions.

Uses.—For *coinage*, mixed with 8·33 per cent. of copper to increase hardness. For *jewellery*; pure gold being regarded as of 24 carats, and English standard gold as of 22 carats (that is, 22 parts of gold in every 24). An 18 carat gold contains $\frac{18}{24}$ or $\frac{3}{4}$ its weight of gold. Gold is also used for *electro-gilding*, a solution of the double cyanide of gold and potassium ($AuCy_3$,KCy) being employed for this purpose. It is also used for coloring glass ruby red ; for gold leaf, wire, etc.

Compounds of Gold (Au=196·7)

		COMPOUNDS.	Formula (General.)	Molecular Weight.
1	Oxides.	Aurous oxide (suboxide)	Au_2O	409·4
2		Auric ,, (peroxide, or auric anhydride)	Au_2O_3	441·4
3		Auric hydrate	AuH_3O_3	
4	Chlorides.	Aurous chloride	$AuCl$	232·2
5		Auric ,, ...	$AuCl_3$	303·2
		(Iodides correspond to chlorides.)		
6	Sulphide.	Auric sulphide	Au_2S_3	489·4

Compounds of Gold and Oxygen.

Aurous oxide ... ... Au_2O.

Auric oxide ... ... Au_2O_3.

(1.) Aurous Oxide; *Suboxide of gold* (Au_2O).

Preparation.—Precipitated on adding a dilute solution of potassic hydrate to one of aurous chloride.

Properties.—A dark powder, soluble in an excess of alkali. A temperature of 302° F. (150° C.) decomposes it into auric oxide and the metal. With hydrochloric acid, the metal and auric chloride are formed ($3Au_2O + HCl = 2AuCl_3 + 3H_2O + 4Au$).

(2.) Auric Oxide; *Peroxide* or *Sesquioxide of gold; Auric anhydride* ($Au_2O_3 = 441{\cdot}2$).

Preparation.—A solution of auric chloride is decomposed by magnesia, a magnesic aurate (MgO,Au_2O_3) being precipitated. If this magnesic aurate be digested with nitric acid, an insoluble auric oxide remains, either as a yellow hydrate ($Au_2O_3,3H_2O$), or as a brown precipitate (Au_2O_3), the exact compound formed being dependent on the strength of the nitric acid employed.

Properties.—Auric oxide is resolved into the metal and oxygen slowly by exposure to light, but instantly by a heat of 473° F. (245° C.). With the alkalies, the hydrated oxide forms soluble salts, called *the aurates*, as *e.g.*, *potassium aurate* ($KAuO_2,3H_2O$), a compound used by electro-gilders. With the earths, and with other metallic oxides, auric oxide forms insoluble compounds. With ammonia it forms a "fulminating gold" ($Au_2O_3,4NH_3,H_2O$?).

Strong nitric and sulphuric acids dissolve it, the oxide being deposited on dilution. With HCl, HI, and HBr, it forms $AuCl_3$, AuI_3, and $AuBr_3$.

COMPOUNDS OF GOLD AND CHLORINE.

Aurous chloride	AuCl.
Auric chloride	$AuCl_3$.

(4.) Aurous Chloride; *Protochloride of gold* ($AuCl = 232{\cdot}2$).

Preparation.—By heating auric chloride to 347° F. (175° C.), until chlorine ceases to be evolved.

Properties.—An insoluble yellow substance, decomposed at 390° F. (200° C.). By the action of boiling water, or by exposure to light, it is converted into the metal and $AuCl_3$.

Aurous Iodide (AuI).

Preparation.—(1.) By the action of hydriodic acid on auric oxide ($Au_2O_3 + 6HI = 2AuI + 3H_2O + 2I_2$).

(2.) By the action of potassic iodide on auric chloride ($AuCl_3 + 3KI = AuI + 3KCl + I_2$).

Properties.—An unstable yellow powder.

(5.) Auric Chloride; *Terchloride of gold* ($AuCl_3 = 303{\cdot}2$).

Preparation.—(1.) By dissolving gold in aqua regia, and evaporating the solution at 248° F. (120° C.).

(2.) By heating gold-leaf in a current of chlorine.

Properties.—A red, deliquescent, crystalline mass. When crystallised from its solution it has the formula $AuCl_3,2H_2O$. Heated to 390° F. (199° C.), it becomes AuCl; but when a higher temperature is applied the compound is decomposed. It sublimes unchanged in an atmosphere of chlorine at a temperature of 572° F. (300° C.). It is soluble in water, in alcohol, and in ether, ether being also capable of removing it from its aqueous solution. Its solution in water stains the skin and other organic matter of a purple color, finely divided gold being deposited. The extreme ease with which the gold of the salt may be reduced, renders it useful in photography.

It forms crystallizable compounds with the alkaline chlorides (such as $AuCl_3,KCl,2H_2O$) called Chlor-aurates, and with the chlorides of most organic bases. With ammonia, it forms a "*fulminating gold.*"

Purple of Cassius.—When a dilute mixed solution of stannous and stannic chloride is added, drop by drop, to a very dilute neutral solution of auric chloride, a purple precipitate is thrown down, the precipitation of which is assisted by the presence of a soluble salt and by the application of heat. This precipitate is called "*the purple of Cassius*" ($Sn''Au_2Sn_2O_6,4H_2O$(?), *i.e.*, a double stannate of gold and tin). This compound may also be prepared by digesting metallic tin in a neutral solution of auric chloride. It is soluble in ammonia, the solution being decomposed and rendered colorless by light, metallic gold being precipitated. The precipitate, mixed with a little borax, is employed for coloring china and porcelain a rich rose red tint. The color is a mixture of metallic gold with stannic oxide.

COMPOUND OF GOLD AND SULPHUR.

Auric sulphide .. .. Au_2S_3.

(6.) Auric Sulphide (Au_2S_3).

Preparation.—By passing sulphuretted hydrogen through a *cold* dilute solution of auric chloride. [By passing sulphuretted hydrogen through a *boiling* solution of auric chloride, metallic gold is precipitated. It was formerly considered to be an aurous sulphide (Au_2S).]

Properties.—A dark-brown substance, soluble in the alkaline sulphides.

A soluble *double sulphide of gold and potassium* may be prepared by heating together gold, sulphur, and potassic carbonate. This compound resists a red heat, and is used for gilding china (*Burgos lustre*).

OXY-SALTS.

Simple oxysalts of gold are not known, but certain double salts (*e.g.*, the double thiosulphate of gold and sodium) are known. Double sulphites, etc., have also been prepared.

REACTIONS OF THE COMPOUNDS OF GOLD.

Non-luminous flame; No color.

1. Heated in the open air, all gold salts are reduced.

2. *Ferrous sulphate* gives in an acid solution (free nitric acid being absent) a brown ppt. of metallic gold.

3. *A mixture of dilute stannous and stannic chloride* (or metallic tin), gives in a neutral solution a ppt. of "purple of Cassius."

4. *Mercurous nitrate* also gives a dark brown ppt. of reduced gold.

5. *Sulphuretted hydrogen;* a black ppt. (Au_2S_3).

Estimation.—Gold is estimated as the metal, precipitated by ferrous sulphate.

PLATINUM (Pt).

Atomic weight, 197·4 (? 194·4). *Specific gravity,* 21·5. *Specific heat,* 0·0311. *Melts at about* 3632° F. (2000° C.). *Atomicity; a dyad in platinous salts* (*e.g.*, $Pt''Cl_2$), *and a tetrad in platinic salts* (*e.g.*, $Pt\ Cl_4$).

History.—Discovered by Wood, of Jamaica, 1741.

Natural History.—It occurs native, in small grains, in the *débris* of the older volcanic rocks, alloyed with palladium, rhodium, iridium, osmium and ruthenium; and sometimes also in larger nodules, alloyed with gold, silver, copper, iron, and lead. It also occurs in certain river sands. It is chiefly found in Russia.

Extraction.—(1.) The ore is first dissolved in dilute aqua regia to separate the gold, and afterwards boiled in concentrated aqua regia, whereby a solution of platinic chloride ($PtCl_4$) is formed. Ammonic chloride is now added to the clear filtrate, by which means the platinum is precipitated as a double chloride of platinum and ammonium ($2NH_4Cl,PtCl_4$), together with any iridium present. This precipitate is now heated, when the ammonia and the chlorine are expelled, and the metal left in a spongy condition. This spongy mass, after being powdered, is forcibly compressed into a solid block, which is then intensely heated and hammered whilst hot, in order to weld the metallic particles together into a solid lump (process of Wollaston).

Deville and Debray have suggested fusing the metal in a lime crucible by the oxy-hydrogen blowpipe, instead of uniting the metallic particles by welding. All impurities, except rhodium and iridium are by this process removed, gold and palladium being volatilized in the metallic state. The sulphur, phosphorus, arsenic and osmium are volatilised as oxides, whilst the iron and copper are first oxidised and afterwards absorbed by the lime crucible.

(2.) Another process suggested by Deville and Debray is as follows:—When platinum ore is roasted with lead sulphide and oxide, the reduced lead dissolves the platinum (together with some iridium and rhodium), an easily fusible alloy of lead and platinum being formed, at the same time that an alloy of iridium and osmium (osmide of iridium), insoluble in the melted lead, sinks to the bottom of the platiniferous lead. The platinum alloy is then ladled away from the insoluble residue, the separation of the lead from the platinum being effected by cupellation. The crude platinum is afterwards refined by fusion, the oxy-hydrogen blowpipe being employed for that purpose. It still, however, retains some iridium and rhodium. These metals are said to improve rather than to injure the platinum for the purposes of chemical apparatus.

Preparation of pure platinum.—Dissolve the platinum in aqua regia and evaporate off the excess of acid. Precipitate the platinum and iridium hydrates from the solution with caustic soda. Add to the precipitate formed a little alcohol, and boil. The platinic hydrate undergoes no change, but the IrH_4O_4 becomes $Ir_2H_6O_6$. Add an excess of hydrochloric acid to this mixed solution, and afterwards ammonic chloride. The Ir_2Cl_6 remains in solution, whilst the platinum is precipitated as ammonium platinic chloride. Collect this insoluble precipitate and ignite.

In preparing "platinum black," platinous chloride ($PtCl_2$) is to be dissolved in a solution of potassic hydrate, and afterwards heated with alcohol. The precipitated platinum black is then collected, washed and dried.

Properties.—(*a.*) *Physical.* A white hard metal, of great tenacity. Its hardness is increased by the presence of iridium. It cannot be crystallised artificially, although native octahedra have been met with. Its specific gravity varies from 21 to 22, according to the process by which it is prepared. It expands very slightly by heat; hence platinum wires may be sealed into glass. It may be fused at 3632° F. (2000° C.) by the oxy-hydrogen blowpipe, or by the galvanic battery. It may be sublimed at a red heat in a current of chlorine, this action being dependent on the formation and decomposition of the chloride. The conducting power of the metal for heat and electricity is inferior to that of either silver or gold. It may be welded.

(β.) *Chemical.* Platinum does not oxidise in the air, dry or moist, at any temperature, but like silver, it absorbs oxygen mechanically when heated, evolving it again on cooling ("Spitting," *see* Silver). Hydrogen passes through, or perhaps is dissolved by the red hot metal. Other gases, such as oxygen, nitrogen, etc., do not possess this property. It is unacted upon by any single acid, but is soluble in nitro-hydrochloric acid and in chlorine water. It corrodes when heated with the caustic alkalies, with the alkaline earths, with nitre, or with the fused alkaline cyanides. At high temperatures it is easily attacked by carbon, arsenic, phosphorus, boron, silicon, etc. It possesses in all forms, but more especially in the spongy condition (platinum black), the remarkable power of inducing chemical combinations between oxygen and other gases, a property dependent on the power of the metal under certain physical conditions for condensing gases on its surface (*see* page 10).

Uses.—It is largely employed in the laboratory, on account of its infusibility, and its power of resisting chemical reagents (*e.g.*, oil of vitriol stills, etc.). It is strongly electro-negative; hence its value in "Grove's battery," where it is combined with zinc for the purpose of generating electricity.

Compounds of Platinum (Pt = 197·4).

		COMPOUNDS.	Formulæ (General.)	Molecular Weight.	Specific Gravity.	Pt per cent.
1	Oxides.	Platinous oxide	PtO	213·4		
2		,, hydrate	PtH_2O_2			
3		Platinic oxide	PtO_2	229·4		
4		,, hydrate	PtH_4O_4			
5	Chlorides.	Platinous chloride	$PtCl_2$	268·4		
6		Platinic ,,	$PtCl_4$	339·4		58·12
7		Potassium platinic-chloride	$2KCl,PtCl_4$	488·3	3·586	40·36
8		Sodium platinic-chloride	$2NaCl,PtCl_4$			
9		Ammonium platinic-chloride	$2NH_4Cl,PtCl_4$	446·4	3·009	44·18
10		[Bromides and iodides analogous to the chlorides]				
11		Platinous sulphide	PtS	229·4		
12		Platinic ,,	PtS_2	261·4		
13	Oxy-salts.	,, sulphate	$Pt(SO_4)_2$			
14		,, nitrate	$Pt(NO_3)_4$			
15		Platinous sulphite	$PtSO_3$			

Compounds of Platinum and Oxygen.

1. Platinous oxide	PtO.
3. Platinic oxide	PtO_2.

(1 and 2.) **Platinous Oxide.**—*Monoxide* or *protoxide* (PtO=213·4).

Preparation.—By decomposing platinous chloride with a solution of potassic hydrate, and afterwards neutralising with sulphuric acid. The precipitated hydrate (PtH_2O_2) is to be collected and *gently* heated, when PtO is formed.

Properties.—A black substance, easily decomposed by heat. It acts as a feeble base, being soluble in acids as well as in excess of an alkali.

(3 and 4.) **Platinic Oxide.**—*Binoxide of platinum* (PtO_2=229·4).

Preparation.—On adding sodium carbonate to a solution of platinic nitrate, the hydrate $PtO_2,2H_2O$ (=PtH_4O_4) is precipitated. [Only one-half of the total quantity of sodium carbonate necessary for complete precipitation should be added, because of the tendency of PtO_2 to combine with alkaline bases.] The platinic hydrate dried at 212° F. (100° C.) leaves PtO_2.

Properties.—The hydrate is brown, and the anhydrous oxide black.

All the oxygen may be expelled from platinic oxide by heat. It acts both as a weak base and as a weak acid (*platinic acid*), the salts (*platinates*) being of a yellowish-red color (*e.g.*, *platinate of soda*, $Na_2O, 3PtO_2, 6H_2O$).

COMPOUNDS OF PLATINUM AND CHLORINE.

5.	Platinous chloride	$PtCl_2$.
6.	Platinic chloride	$PtCl_4$.

(5.) **Platinous Chloride.**—*Protochloride of platinum* ($PtCl_2=268{\cdot}4$).

Preparation.—By evaporating a solution of platinum in aqua regia to dryness, and heating the residue at 455° F. (235° C.) until chlorine ceases to be evolved.

Properties.—An olive-green powder, soluble in a potash solution, in hot hydrochloric acid (the solution being red), and in a solution of platinic chloride (the solution being brown). It is insoluble in water, in nitric or in sulphuric acids. Heat decomposes it. It combines directly with unsaturated hydrocarbons like ethylene (C_2H_4).

Chloro-platinites.—With the alkaline chlorides, platinous chloride forms double salts called *chloro-platinites*, or *platinoso-chlorides*.

(6.) **Platinic Chloride.**—*Tetrachloride*, *perchloride* or *bichloride of platinum* ($PtCl_4=339{\cdot}4$).

Preparation.—By dissolving platinum in aqua regia, and evaporating the solution so formed to dryness.

Properties.—A brownish-red, crystalline, deliquescent salt ($PtCl_4, 5H_2O$), soluble in alcohol, in ether and in water, the aqueous solution presenting a deep orange color. Heated to 455° F. (235° C.) it becomes $PtCl_2$, but when a temperature above this is employed, the platinous chloride is decomposed, and the metal set free. Sulphurous acid reduces $PtCl_4$ to $PtCl_2$.

When platinic chloride is crystallized from an hydrochloric acid solution, a compound having the formula $PtCl_4, 2HCl, 6H_2O$ separates.

Chloro-platinates.—With certain metallic chlorides (such as the chlorides of the alkalies and the alkaline earths), $PtCl_4$ forms double salts called *chloro-platinates*, or *platino-chlorides*, having the general formula $2M'Cl, PtCl_4$. The potassium and ammonium platino-chlorides ($2KCl, PtCl_4$, and $2NH_4Cl, PtCl_4$) are but very slightly soluble in water, and insoluble in alcohol. They constitute, therefore, the compounds by which the ammonia or the potassium present in a solution may be estimated. Both the potassium and ammonium platino-chlorides consist of yellow octahedral crystals. The ammonium salt is easily decomposed by heat, but the potassium salt undergoes decomposition with difficulty. The sodium compound is, on the contrary, of a red color, and very soluble both in water and in alcohol. Platinic chloride also forms double salts with the chlorides of some of the organic bases.

PLATINAMINES.

Bases Produced by the Action of Ammonia on Platinum Chlorides.

These bases, of which several have been described, are to be regarded as ammonias, in which part of the hydrogen of two or more ammonia molecules has been replaced by platinum, either in the form of dyad or tetrad platinum.

Similar, but less important groups occur in the case of cobalt (*cobalt-amines*), and perhaps of copper and mercury. Four only of the ammonia compounds of platinum will be noted here :—

(1.) **Platoso-Tetrammonic Chloride** (*Chloride of Reiset's first base*) has the formula $\mathrm{Pt}''\left\{\begin{matrix}\mathrm{NH_2(NH_4)Cl}\\ \mathrm{NH_2(NH_4)Cl}\end{matrix}\right.+\mathrm{H_2O}$. It is prepared by dissolving platinous chloride in an excess of ammonia and evaporating the solution.

With platinous chloride this compound forms *the green salt of Magnus*,

$$\mathrm{Pt}''\left\{\begin{matrix}\mathrm{NH_2(NH_4)Cl}\\ \mathrm{NH_2(NH_4)Cl}\end{matrix}\right.+\mathrm{PtCl_2}.$$

On adding argentic sulphate to a solution of the chloride, a platoso-tetrammonic sulphate is formed.

If barium hydrate be added to a solution of the sulphate, **Platoso-tetrammonic hydrate** is formed, $\mathrm{Pt}''\left\{\begin{matrix}\mathrm{NH_2(NH_4)HO}\\ \mathrm{NH_2(NH_4)HO}.\end{matrix}\right.$ This base is a strong caustic and deliquescent alkali. Like the alkaline hydrates, it absorbs carbonic acid from the air, and expels ammonia when added to its salts.

(2.) **Platoso-Diammonic Chloride** (*Chloride of Reiset's second base*) has the formula $\mathrm{Pt}''\left\{\begin{matrix}\mathrm{NH_3Cl}\\ \mathrm{NH_3Cl}.\end{matrix}\right.$ It is prepared by heating the platoso-tetrammonic chloride to 518° F. (270° C.).

By heating the platoso-tetrammonic hydrate to 230° F. (110° C.), the platoso-diammonic hydrate is formed, $\mathrm{Pt}''\left\{\begin{matrix}\mathrm{NH_3.HO}\\ \mathrm{NH_3.HO}.\end{matrix}\right.$ This base forms insoluble but easily decomposed salts with acids.

(3.) **Platino-Diammonic Chloride** (*Chloride of Gerhardt's base*) has the formula $\mathrm{PtCl_2}\left\{\begin{matrix}\mathrm{NH_3Cl}\\ \mathrm{NH_3Cl}.\end{matrix}\right.$ It is prepared by passing chlorine through water in which the platoso-diammonic chloride is suspended.

The hydrated base is formed on adding ammonia to a boiling solution of the nitrate. It has the same composition as that assigned to fulminating platinum.

(4.) **Platino-Tetrammonic Chloride** (*Gros' chloride*) has the formula $\mathrm{PtCl_2}\left\{\begin{matrix}\mathrm{NH_2(NH_4)Cl}\\ \mathrm{NH_2(NH_4)Cl}.\end{matrix}\right.$ It is prepared by heating the platino-diammonic chloride with ammonia.

Compounds of Platinum and Sulphur.

(12.) Platinous sulphide ... ... PtS.
(13.) Platinic sulphide ... ... PtS_2.

(12, 13.) These sulphides are formed by the action of sulphuretted hydrogen on platinous and platinic chlorides respectively. Platinic sulphide is also formed when sulphuretted hydrogen is passed through a solution of a platinum compound. Platinic sulphide is soluble in the alkaline sulphides and hydrates, forming the *sulpho-platinates.*

Platino-nitrites.—These are compounds of platinum with nitrites of other metals, *e.g.*, $K_2Pt(NO_2)_4$. The platinum cannot be detected in these bodies by the usual reagents, nor do they behave like ordinary double salts.

Reactions of Platinum Compounds.

Platinic Salts.

1. *Sulphuretted hydrogen;* a black ppt. (PtS_2), soluble in excess of ammonic sulphide.
2. *Ammonia;* a yellow ppt. ($2NH_4Cl,PtCl_4$), decomposed by heat.
3. *Potassic hydrate;* a yellow ppt. ($2KCl,PtCl_4$).
4. *Stannous chloride;* a deep brown in acid solutions.
5. *Potassic iodide;* a brown ppt. of PtI_4.

Estimation of Platinum.—(1.) As a metal.

(2.) As the potassic or ammonic platinic chloride—

$$100\ (2KCl,PtCl_4) = 40{\cdot}36\ Pt.$$
$$100\ (2NH_4Cl,PtCl_4) = 44{\cdot}18\ Pt.$$

MOLYBDENUM (Mo).

Atomic weight, 96. *Atomicity: dyad in molybdous compounds* (*as* $Mo''Cl_2$; $Mo''O$), *and tetrad in molybdic compounds* (MoO_2; $MoCl_4$). *Specific heat,* 0·0722.

History.—Discovered by Hjelm, 1782. Formerly the atomic weight was stated as 92, but Mendeleef predicted that it would be found to be above 94, the atomic weight of Niobium. This prophecy has been confirmed by later experiments.

Natural History.—The metal is not found free in nature, but occurs chiefly as a *sulphide* (called molybdena (μολύβδαινα) from its resemblance to black-lead) in molybdenite (MoS_2), as an *oxide* in molybdenum ochre (MoO_3), and as a *lead molybdate* in wulfenite ($PbMoO_4$).

Preparation.—By the reduction of MoO_2 in a current of hydrogen, or by the action of a very high temperature on a mixture of the oxide with carbon.

Properties.—A white, brittle metal, permanent in air at ordinary temperatures. Infusible in the oxyhydrogen flame unless the metal contains carbon. Specific gravity, 8·6. The metal is oxidized to molybdic acid (H_2MoO_4) by boiling it in nitric acid. It is soluble in hot sulphuric acid, but is insoluble in dilute nitric and hydrochloric acids. By heat it combines with chlorine ($MoCl_4$) the product being evolved in the form of red vapors, which condense to black scales. It also combines with oxygen, molybdic oxide (MoO_3) being formed when the metal is heated to redness. Molybdenite marks paper with an olive green streak.

Compounds of Molybdenum (Mo = 96).

		COMPOUNDS.	Formulæ (General).	Molecular Weight.
1	Oxides.	Hypomolybdous oxide	MoO	112
2		Molybdenum sesquioxide	Mo_2O_3	240
3		Molybdous oxide	MoO_2	128
4		Molybdic oxide (anhydride)	MoO_3	144
5		Molybdic acid	H_2MoO_4	
6		Phospho-molybdic acid	$H_3PO_4.11MoO_3$	
7	Chlorides.	Hypomolybdous chloride	$MoCl_2[MoBr_2]$	167
8		Molybdenum sesquichloride	$Mo_2Cl_6[Mo_2Br_6]$	405
9		Molybdous chloride	$MoCl_4[MoI_4]$	238
10		Molybdic ,,	$MoCl_5$	273·5
11		Molybdenum oxychlorides	$MoOCl_4$	244
12			MoO_2Cl_2	
13			$Mo_2O_3Cl_6$	
14	Sul-phides.	Molybdous sulphide	MoS_2	160
15		Molybdic ,,	MoS_3	192
16		,, persulphide	MoS_4	224
17		Sulphomolybdic acid	H_2MoS_4	
18		Persulphomolybdic acid	H_2MoS_5	

(1.) Hypomolybdous Oxide (MoO).

Preparation.—By the action of potassium hydrate on $MoCl_2$. A black powder.

(2.) Molybdenum Sesquioxide (Mo_2O_3).

Preparation.—By the action of heat on the hydrate ($Mo_2H_6O_6$) precipitated when a caustic alkali is added to a solution of Mo_2Cl_6, air being excluded.

A grey powder, insoluble in acids.

(3.) Molybdous Oxide (MoO_2).

Preparation.—By heating the hydrate (MoH_4O_4) precipitated on adding ammonia to a solution of $MoCl_4$ in the absence of air. A brown powder, insoluble in water, in hydrochloric acid or in potash. Oxidised by nitric acid to molybdic acid.

(4.) Molybdic Oxide or Anhydride (MoO_3).

Preparation. (See above.) Also by roasting MoS_2, and by heating ammonic molybdate in air.

Properties.—A white powder, becoming yellow when heated. Fuses and sublimes. Soluble in ammonia and in the fixed alkalies. Insoluble in acids.

Molybdic Acid.—The Molybdates.

(5.) Molybdic Acid (H_2MoO_4).

Preparation.—By adding hydrochloric or nitric acid (avoiding excess of acid) to a solution of a molybdate.

Properties.—A yellow crystalline powder, insoluble in water, soluble in excess of acid. When zinc is added to a hydrochloric acid solution, the nascent hydrogen evolved effects a reduction of the molybdic acid, a colored solution, changing from blue to green and finally to dark brown, resulting.

Molybdic acid (H_2MoO_4) is dibasic. Thus K_2MoO_4 is the normal potassic molybdate. It also forms acid salts.

There are several hydrates of MoO_3, rendering the molybdates a class of considerable complexity.

The ammonium molybdate used in the laboratory as the test, both qualitative and quantitative, for phosphoric acid, has the composition $(NH_4)_6Mo_7O_{24},4H_2O$. To a solution containing phosphoric acid, an excess of ammonic molybdate dissolved in strong ammonia (since the salt is decomposed by water) is added. When the solution, acidulated with nitric acid is heated, a yellow precipitate, insoluble in water or in dilute acids, but easily soluble in ammonia, is formed. This precipitate consists of the ammonic phospho-molybdate [$(NH_4)_3PO_4,11MoO_3,6H_2O$], and contains all the phosphoric acid previously in solution.

The alkaline molybdates, and the molybdates of zinc and magnesium, are soluble in water. The molybdates of barium, strontium and calcium are only slightly soluble.

Phospho-molybdic Acid.—The Phospho-Molybdates.

(6.) Phospho-molybdic Acid ($H_3PO_4,11MoO_3,12H_2O$).

Preparation.—By boiling ammonic phospho-molybdate ($(NH_4)_3PO_4,11MoO_3,6H_2O$) (see above) in aqua regia, the resulting solution being allowed to evaporate spontaneously.

Properties.—Soluble in water. Crystallizes in yellow prisms.

(NOTE.—Ammonium molybdate produces a yellow salt with an acid solution of arsenic acid or of an arsenate.)

(7 to 10.) The Chlorides of Molybdenum.—By heating molybdenum in chlorine, *molybdic chloride* ($MoCl_5$), may be obtained. (Fuses at 381·2° F. (194° C.); fumes on exposure to air.)

By heating molybdic chloride ($MoCl_5$) to 482° F. (250° C.) in a current of hydrogen, *molybdenum sesquichloride* (Mo_2Cl_6) is obtained.

By heating molybdenum sesquichloride (Mo_2Cl_6), *molybdous chloride*, $MoCl_4$, is obtained.

By heating molybdenum sesquichloride (Mo_2Cl_6) in a current of carbonic anhydride, *hypomolybdous chloride* ($MoCl_2$) is obtained.

(15 to 17.) The Sulphides of Molybdenum.—*Molybdous Sulphide* (MoS_2) is prepared by heating molybdic oxide (MoO_3) in a current of H_2S. *Molybdic Sulphide* (MoS_3) is prepared by adding HCl to a molybdate solution saturated with H_2S. *Molybdic Persulphide* (MoS_4) is prepared by first boiling a solution of potassium molybdate saturated with sulphuretted hydrogen, and afterwards adding hydrochloric acid to the solution of potassic persulphomolybdate formed (K_2MoS_5).

TESTS FOR MOLYBDENUM COMPOUNDS.

(A.) Tests for MOLYBDOUS SALTS (corresponding to $Mo''O$); *color*, black and opaque.

(B.) Tests for MOLYBDIC SALTS (corresponding to $Mo^{iv}O_2$); *color*, reddish brown.

(1.) *Sulphuretted hydrogen;* at first a blue tint, and then a brown ppt., soluble in ammonic sulphide.

(2.) *Sodic and potassic hydrates and their carbonates;* a brown ppt., soluble in ammonic carbonate.

(C.) Tests for MOLYBDATES.

(1.) A piece of zinc placed in a dilute acid solution of a molybdate, turns the liquid first blue, then green, and finally black.

(2.) *Stannous chloride;* a blue ppt. ($MoO_2,4MoO_3$).

(3.) *Acids;* a ppt. of MoO_3, soluble in excess.

(4.) *Potassic Ferrocyanide* ; a reddish-brown ppt.

All molybdenum compounds color a borax bead dark brown in the inner flame, and yellow in the outer flame. The color of the bead disappears on cooling.

IRIDIUM (Ir).

Atomic weight, 198. *Specific gravity*, 22·38. *Atomicity, dyad* (IrO); *tetrad* ($IrCl_4$); *pseudo-triad* (Ir_2Cl_6).

History.—Discovered by Smithson Tennant, 1804. Called iridium (*iris*, the rainbow) on account of the varied tints of its compounds.

Natural History.—Found native in most platinum ores. It also occurs as an alloy with osmium (*osmiridium*).

Preparation.—(1.) (*α*.) Chlorine is first passed over a heated mixture of the iridium alloy (iridium, ruthenium and osmium) with sodium chloride, double chlorides of iridium and sodium ($2NaCl,IrCl_4$) and of osmium and sodium, etc., being formed.

(*β*.) This mass is now treated with boiling water, whereby the double chlorides formed are dissolved away from the insoluble portion (ruthenium not being soluble).

(*γ*.) The concentrated solution is then distilled with nitric acid, which decomposes the double osmium salt, liberating the volatile osmic anhydride (OsO_4).

(δ.) The solution remaining in the retort (which contains the iridium) is then treated with ammonium chloride, and the resulting dark red-brown precipitate of ammonium iridic chloride ($2NH_4Cl, IrCl_4$) ignited. In this way iridium is obtained in a spongy form. (Wöhler.)

(2.) Frémy prepares the metal by igniting the potassium iridic chloride ($2KCl,IrCl_4$) in a current of hydrogen. The double chloride is formed by the action of potassium chloride on a solution of the metal in aqua regia ($IrCl_4$).

Properties.—(α.) *Physical.* A hard, white and brittle metal, crystallizing in cubes as well as in six-sided prisms (*dimorphous*). The metal may be obtained as a black powder, by precipitating it with alcohol from a solution of the sulphate. This finely divided iridium possesses properties similar to, but more energetic than platinum black. It fuses when heated in the voltaic arc or in the oxyhydrogen jet.

The fused metal has a specific gravity of 22·38.

Its alloy with osmium has a specific gravity of 22·6. The metal is sometimes used for tipping gold pens.

(β.) *Chemical.* The pure metal in mass is unacted upon either by air, by heat, or by any acid. On the contrary, the alloy of iridium and platinum is soluble in aqua regia, whilst the finely divided metal when heated in air absorbs oxygen, forming the sesquioxide (Ir_2O_3), a black powder used for imparting an intense black to porcelain. The finely powdered metal is oxidized (but not dissolved as in the case of rhodium) by fusion with hydric potassic sulphate. It is also oxidized by fusion with sodic nitrate and sodic hydrate, the resulting compound being soluble in aqua regia, forming a deep black solution containing the double sodium iridic chloride ($2NaCl,IrCl_4$). Iridium, like palladium, combines with carbon when heated in the flame of a spirit lamp.

Compounds of Iridium (Ir = 198).

COMPOUNDS.		Formulæ.	Molecular Weight.
Oxides.	Iridous oxide	IrO	214
	Iridic sesquioxide	Ir_2O_3	444
	,, dioxide	IrO_2	230
	,, hydrate	IrH_4O_4	266
	,, anhydride	IrO_3	246
Chlorides.	Iridous chloride	$IrCl_2$	269
	Iridic sesquichloride	Ir_2Cl_6	609
	,, chloride	$IrCl_4$	340
	(The iodides similar to the chlorides).		
Sulphides.	Iridous sulphide	IrS	230
	Iridic sesquisulphide	Ir_2S_3	492
	,, sulphide	IrS_2	262

Iridic Chloride ($IrCl_4$). *Preparation.*—By dissolving the metal or its sesquioxide in aqua regia.

The chloride forms double salts with alkaline chlorides, isomorphous with the platinum salts (*e.g.*, the potassium iridic chloride $2KCl,IrCl_4$).

REACTIONS.

(1.) *Sulphuretted hydrogen* first decolorizes a solution of $2NaCl,IrCl_4$ precipitating sulphur, and afterwards precipitates the brown Ir_2S_3.

(2.) *Ammonic sulphide;* reaction as above, the precipitated Ir_2S_3 being soluble in excess.

(3.) *Sodic or potassic hydrate;* a brownish black precipitate, the solution turning green, and when heated blue.

(4.) *Potassic chloride;* a dark brown precipitate ($2KCl,IrCl_4$).

(5.) Zinc precipitates spongy iridium from solutions of its salts.

CHAPTER XVIII.

THE METALS OF GROUP I.

LEAD and its Compounds—SILVER and its Compounds—MERCURY and its Compounds—THALLIUM and its Compounds—TUNGSTEN and its Compounds.

LEAD ($Pb = 206{\cdot}5$).

Atomic weight, 206·5. *Specific gravity*, 11·445. *Specific heat*, 0·0314; *Fuses*, 617° F. (325° C.). *Atomicity: dyad* ($PbCl_2$)*; tetrad* (PbO_2; $Pb(C_2H_5)_4$), *and occasionally a pseudo-triad* ($'Pb'''_2(C_2H_5)_6$).

History.—Known to the ancients (*Plumbum*) (♄ = scythe of Saturn. Hence the expression "Saturnine poisoning.")

Natural History.—Not found native, or at most in very minute quantities. Occurs chiefly as a *sulphide* (galena) (PbS), accompanied by more or less silver. In smaller quantities it is found as a *carbonate*, "white lead ore" (cerussite) ($PbCO_3$), and as a *sulphate* ("anglesite") ($PbSO_4$). A phosphate, tungstate, oxychloride, molybdate, arsenate, and chromate of lead occur as native minerals.

Preparation.—*From Galena.*—1. (*a.*) The ore, after the addition of a little lime, is roasted in a reverberatory furnace with free access of air. The following changes take place :—One part of the PbS becomes oxidized to $PbSO_4$; a second part loses its sulphur (with evolution of SO_2), PbO being formed ; a third part remains undecomposed. Thus a mixture of $PbSO_4$, PbS and PbO results.

(*β.*) Air being excluded, the heat of the furnace is now raised. The following changes occur :—The sulphate and oxide of lead respectively decompose the unaltered lead sulphide, the metal being reduced with evolution of SO_2. Thus—

(*a.*) $PbSO_4 + PbS = 2Pb + 2SO_2$.
Lead sulphate + Lead sulphide = Lead + Sulphurous anhydride.

(*β.*) $2PbO + PbS = 3Pb + SO_2$.
Lead oxide + Lead sulphide = Lead + Sulphurous anhydride.

In some cases carbon (partially burnt peat) is added to assist in the reduction of the ore.

[During the operation of roasting some plumbous sulphide (Pb_2S) is formed (fusible matt), which floats on the metal, and has to be re-treated.]

2. Where other metallic sulphides (as ZnS or FeS) are present, the

ore may be reduced by fusion with cast iron, the quantity of iron added being less than is required by the sulphur of the PbS. The sulphur combines with the iron to form ferrous sulphide, it having a greater attraction for iron than for lead. This, with any other sulphides that may be formed, float as a fusible slag on the top of the molten lead.

3. *Preparation of pure lead.*—The pure nitrate is to be ignited, and the oxide formed reduced with black flux.

Impurities.—Antimony (forming "*hard lead*"), manganese, silver, tin, iron, copper.

Purification ("*Refining*," "*Improving*," "*Softening*").—The lead is first melted. The tin and antimony present (which render the lead hard) oxidize more rapidly than the lead. These oxides, as fast as they are formed, must be removed from the surface of the melted metal.

Extraction of Silver.—(1.) *Concentration of the silver alloy by Pattinson's process.*—This process (which is resorted to if the silver present be less than one-tenth per cent. of the alloy) depends on the circumstance that the alloy of silver and lead is more fusible than pure lead. The lead containing the silver is melted in iron pots, and well stirred as it cools. A lead, almost entirely free from silver, solidifies and sinks to the bottom of the vessel in the form of crystalline grains, which are ladled out as fast as they are formed. The silver remains in the liquid metal, which at the end of the process, conducted in a series of vessels, usually amounts to about one-third of the lead melted.

(2.) The silver is obtained from this concentrated argentiferous alloy (or directly from the lead without concentration if the silver present be above one-tenth per cent.) by "*cupellation*," as follows :—The alloy is exposed to a high temperature in a free current of air, whereby litharge (PbO) is formed, the silver remaining unchanged. This PbO, which fuses at a low temperature, is run off from the silver, which thus remains of a bright appearance (fulguration) and in a state of comparative purity.

(3.) In Parke's process, advantage is taken of the circumstance that zinc forms an alloy with silver but not with lead. After the silver-lead has been melted, zinc is added to the alloy. The zinc, as soon as it is melted, floats on the surface of the lead, carrying the silver with it. The silver-zinc alloy is removed during solidification, and the zinc dissolved away from the silver by the action of dilute sulphuric acid.

Properties.—(*a.*) *Physical.* Lead is a bluish-white metal, very soft when pure, lustrous when freshly cut. Its softness is more or less destroyed by the presence of plumbic oxide, a small quantity of which is soluble in the melted metal. It is neither very malleable nor ductile. By slow cooling it may be obtained in cubes and octahedra. By the electrolysis of, or by suspending a piece of zinc in, a solution of one of its salts, the lead may be obtained in leaf-like forms. At 617° F. (325° C.) it fuses, and at a white heat boils and volatilizes. It contracts considerably at the moment of solidification. It is inferior to most metals as a conductor of heat or electricity.

(*β.*) *Chemical. Action of Air.*—A perfectly dry air has no action on lead at ordinary temperatures, but the metal rapidly tarnishes in moist air, the film of oxide which forms on the surface preventing the further action of air. At high temperatures the metal rapidly absorbs oxygen, emitting white fumes of lead oxide, and at the same time volatilizing slightly. It becomes covered moreover with a black film of suboxide, which at a higher temperature becomes the yellow oxide ($2PbO,H_2O$).

Action of Water only.—Pure and un-aërated water has no action on pure lead. Lead decomposes water at a white heat with evolution of hydrogen and the formation of PbO.

Action of Air and Water.—Lead rapidly oxidizes (forming PbH_2O_2) from the combined influence of air and water, the water dissolving the hydrated oxide formed, and leaving a clean surface of lead for the further action of the air. The resulting solution of oxide absorbs carbonic anhydride from the air, a basic lead carbonate being precipitated ($PbCO_3,PbH_2O_2$). The water, thus freed from lead, is then capable of dissolving any fresh lead oxide that may be formed on the surface of the metal. By this means the almost complete corrosion of metallic lead (as, *e.g.*, in old leaden coffins) may be effected, with the conversion of the lead into a basic carbonate.

The *circumstances influencing this combined action of air and water on lead* are both numerous and important, viz.:—

1. The presence of chlorides, nitrates, and nitrites, and of ammonia in the water *promote* corrosion.

2. The presence of sulphates, phosphates and carbonates, especially of calcic carbonate in water containing CO_2, *hinder* corrosion. The presence of a *limited quantity* of carbonic acid in water interferes with corrosion, by fixing on the lead a film of insoluble plumbic carbonate; whilst *an excess* of CO_2 may increase corrosion, plumbic carbonate being soluble in water highly charged with the gas. On boiling, the soluble lead carbonate subsides as the gas escapes. The presence of vegetable matter in water also hinders corrosion, by coating the metal with a compound of lead oxide and organic matter. In contact with air and sea-water an oxide and a chloride of lead are formed. Calcic sulphate, in the presence of moisture, rapidly corrodes lead. This is seen when lead pipes are placed in contact with plaster.

The author in a joint paper with Crookes and Odling has shown that the solvent action of soft waters for lead depends on the quantity of dissolved silica and the formation on the lead of a lead silicate, those waters that act freely and continuously on lead invariably containing a very small relative amount of silica in solution. (*See* paper "*On the Action of Soft Waters on Lead,*" by Crookes, Odling, and Tidy, 1887.)

Action of Acids.—Sulphuric acid and hydrochloric acid are without action on lead at ordinary temperatures. Even when boiling, their action is slight. Hot aqua regia acts readily on the metal, crystals of $PbCl_2$ being deposited on cooling. Nitric acid (especially if dilute) dissolves it, nitric oxide being liberated. Acetic acid dissolves the metal rapidly, changing it, in the presence of carbonic acid, to white lead. Hence green oakwood (which contains acetic acid) should never be placed near lead fittings, nor should metallic lead be allowed to remain in contact with acid liquids used as food.

Action of Alkalies.—These possess no special action on lead.

Chlorine acts on lead, until a sufficiently protective covering of lead chloride has been formed.

Uses.—For alloys, as type-metal [Pb(2)Sb(1)Sn(1)], shot (0·5 per cent. of arsenic being added to facilitate the metal assuming a spherical shape), solder (Pb and Sn), etc. The metal is largely used in building operations, as, *e.g.*, for cisterns, roofing, etc.; also for sulphuric acid chambers, etc.

Compounds of Lead (Pb = 207).

	COMPOUNDS.	Formulæ.	Molecular Weight	Specific Gravity.	Pb or PbO per cent.
Oxides.	Plumbous oxide (black sub-oxide)	Pb_2O	430		
	Plumbic oxide (litharge)	PbO	223	9·2 to 9·5	Pb 92·8
	Plumbic peroxide	PbO_2	239	9·45	Pb 86·61
	Red leads	PbO,PbO_2			
		$2PbO,PbO_2$			
		$3PbO,PbO_2$			
	Plumbic chloride	$PbCl_2$	278	5·8	Pb 74·46
xy-chlorides.	Mendipite	$2PbO,PbCl_2$			
	(Pattinson's white)	$PbO,PbCl_2$			
	(Turner's yellow)	$7PbO,PbCl_2$			
	Plumbic bromide	$PbBr_2$	367	6·63	
	Plumbic iodide	PbI_2	461	6·384	
	Plumbic fluoride	PbF_2			
phides.	Plumbous sulphide (subsulphide)	Pb_2S	446		
	Plumbic sulphide (galena)	PbS	239	7·59	Pb 86·61
	Sulphochlorides	$PbS,PbCl_2$			
		$3PbS,PbCl_2$			
	Selenide	$PbSe$			
	Sulphate	$PbSO_4$	303	6·3	PbO 73·6
	Sulphite	$PbSO_3$			
Nitrates.	Plumbic nitrates	$Pb2NO_3$	331	4·4	PbO 67·37
		$Pb2NO_3,PbH_2O_2$			
		$2(Pb2NO_3,2PbO),3OH_2$			
		$Pb2NO_3,5PbO,OH_2$			
	Phosphate (pyro)	$Pb_2P_2O_7$			
	Carbonate	$PbCO_3$	267	6·46	
tates.	Normal acetate	$Pb2(C_2H_3O_2)$			
	Basic acetate	$Pb2(C_2H_3O_2),2PbO$			

COMPOUNDS OF LEAD AND OXYGEN.

1. Plumbous oxide	Pb_2O.
2. Plumbic oxide	PbO.
3. Plumbic peroxide	PbO_2.
4. Red leads	Pb_2O_3 ; Pb_3O_4 ; Pb_4O_5.

(1.) Plumbous Oxide.—*Suboxide of lead* (Pb_2O).

Preparation.—(1.) By heating plumbic oxide to redness.

(2.) By heating lead oxalate to 608° F. (320° C.), air being excluded:—

$$\begin{array}{cccc} 2PbC_2O_4 & = & Pb_2O & + \ 3CO_2 + CO. \\ \text{Lead oxalate} & & \text{Plumbous oxide.} & \end{array}$$

Properties.—A grey substance, which does not combine nor form salts with acids. Plumbic oxide and the metal are formed when plumbous oxide is acted upon by acids or heated in the absence of air.

(2.) Plumbic Oxide.—*Lead protoxide* or *monoxide*; *litharge*; *massicot* (PbO).

Although found in nature, plumbic oxide is a comparatively rare mineral.

Preparation.—(1.) *As a hydrate* ($2PbO,H_2O$ and $3PbO,H_2O$). By precipitating lead solutions with alkalies.

(2.) *Anhydrous* (PbO). By heating lead in air. (*See below.*)

[Most of the commercial litharge is that formed during the cupellation of argentiferous lead.—*See* page 521.]

(3.) By igniting the carbonate, nitrate or hydrate.

Properties.—(*a.*) *Physical.* Lead oxide is found of various colors. It is *yellow*, if the heat used in its preparation be below that necessary to fuse the oxide (massicot); whilst it is *red* (due to the formation of Pb_2O_3) if the heat employed has been great (litharge). Litharge, when heated, turns brown, the color disappearing as the oxide cools. It fuses at a bright red heat. Specific gravity, 9·5.

(β.) *Chemical.* Litharge is slightly soluble in water, solution being *favored* by the presence of organic matter in the water, and *hindered* by the presence of saline constituents. The solution is alkaline. It dissolves freely in nitric and acetic acids. It absorbs CO_2 from the air with great rapidity, a lead carbonate being precipitated. It is a powerful base, and exhibits a great tendency to form basic salts. Most plumbic salts are insoluble in water. Hence lead acetate is in constant use as a laboratory reagent for the detection of acids. At the temperature of fusion, PbO combines with silica or with clay (*e.g.*, clay crucibles) to form a fusible silicate of lead. Plumbic oxide is easily reduced by heat in the presence of organic matter, or in a current of carbonic oxide at 212° F. (100° C.), or in hydrogen at 590° F. (310° C.).

It is soluble in alkaline solutions, forming, with the alkalies, compounds that are easily decomposed.

Uses.—Nearly all the lead salts are prepared from litharge. It is used as a glaze for earthenware. Also in the manufacture of glass, on account of the ease with which it combines with silica at a high temperature. For a flux. Also in the manufacture of "dhil mastic" (a mixture of lead oxide and brickdust, made into a paste with linseed oil), a compound which sets very hard, and is used for repairing stone. It is employed as a hair dye (a solution of the oxide in lime-water), the sulphur of the hair forming the black PbS with the lead.

Plumbic Hydrates.—Hydrates, one having the composition $2PbO,H_2O$ [prepared by the addition of an alkaline hydrate to a salt of lead], and a second, $3PbO,H_2O$ are known. Both are insoluble in water, but readily combine with acids, even with CO_2. No hydrate of the formula PbO,H_2O has been prepared.

(3.) **Plumbic Peroxide** or *Dioxide.—Puce* or *brown lead oxide* (PbO_2) [Mol. wt., 239; Sp. gr., 9·4]. This compound is found native as heavy lead ore or plattnerite.

Preparation.—(1.) By digesting red lead ($2PbO,PbO_2$) in boiling dilute nitric acid, a solution of nitrate of lead is formed and plumbic peroxide (PbO_2) precipitated.

(2.) By fusing together litharge, potassic chlorate and nitre.

(3.) By passing chlorine through water containing plumbic hydrate or carbonate in suspension.

(4.) Deposited on the positive electrode when a lead salt is electrolysed.

Properties.—A brown substance insoluble in water and in acids. It is decomposed at a red heat ($2PbO_2 = 2PbO + O_2$). It acts as a powerful oxidizing agent; hence its use in the manufacture of lucifer matches for igniting the sulphur, and in the laboratory as an absorbent of SO_2 ($PbO_2 + SO_2 = PbSO_4$). Nitric acid has no action upon it. With hydrochloric acid it forms lead chloride, and with sulphuric acid lead sulphate, chlorine being evolved in the former case, and oxygen in the latter. Its properties being feebly acid rather than basic, it has been called *plumbic acid,* and the compounds formed by fusing it with caustic soda or potash, *plumbates.* Thus it combines with alkalies, as in the salt potassic plumbate ($K_2O,PbO_2,3H_2O$). In certain storage batteries the negative plate consists of a porous mass of this material.

(4.) **Red Lead** (*Minium*).—This substance is represented by various formulæ. Pb_3O_4 represents the ordinary and more common formula for red lead, and Pb_2O_3 or Pb_4O_5 the formulæ of the red leads less frequently formed or mixed with the Pb_3O_4 in varying small percentages.

Preparation.—By exposing massicot (*i.e.,* plumbic oxide which has not been fused) to a faint red heat of 608° F. (320° C.) for some hours in the presence of air.

Properties.—A heavy red powder (Sp. gr. 9·08), evolving oxygen when heated ($2Pb_3O_4=6PbO+O_2$). Most acids decompose it, forming plumbic salts and plumbic peroxide. Dilute nitric acid acts upon it in the cold, forming lead nitrate and leaving PbO_2 undissolved. Warmed with hydrochloric acid, it forms lead chloride and evolves chlorine. When strongly heated with sulphuric acid it gives off oxygen, lead sulphate being formed.

Uses.—As a pigment in the manufacture of flint glass. The excess of oxygen in the compound combusts any organic matter present, which would otherwise blacken the glass by reducing the lead. Further, for glass work it is important that the lead oxide be very pure, for if other metallic oxides were present, they would certainly effect a certain discoloration of the glass. It is also used for electrical storage batteries.

Compounds of Lead and Chlorine, etc.

5. Plumbic chloride ... ... $PbCl_2$.
6 to 8. Plumbic oxychlorides ... ... $\begin{cases} PbO, PbCl_2. \\ 2PbO, PbCl_2. \\ 7PbO, PbCl_2. \end{cases}$

(5.) **Plumbic Chloride** ($PbCl_2$) [Mol. wt., 278 ; Sp. gr., 5·8] is found native as "horn-lead," also as cotunnite.

Preparation.—(1.) By precipitating plumbic nitrate with hydrochloric acid or a soluble chloride. (2.) By dissolving the metal in hot aqua regia and allowing the solution to cool. (3.) By dissolving the oxide or carbonate in hydrochloric acid.

Properties.—A white substance, somewhat insoluble in cold water (1 in 130), but soluble in boiling water (1 in 33), from which solution it is deposited on cooling in white rhombic needle crystals. It fuses when heated in vacuo into a horny mass, which at a higher temperature volatilizes. In the presence of air, oxychlorides are formed by the action of heat upon it.

(6 to 8.) There are several **Oxychlorides** of lead ; *e.g.*, (1.) **Pattinson's white oxychloride** ($PbO,PbCl_2$) is a compound used as a substitute for white lead. It is prepared by adding lime-water to a solution of $PbCl_2$ in hot water ($2PbCl_2+CaO=PbO,PbCl_2+CaCl_2$). (2.) **Mendipite** ($2PbO,PbCl_2$). (3.) **Turner's yellow** (Paris, patent or mineral yellow) ($7PbO,PbCl_2$), is prepared by heating together litharge and ammonium chloride.

(10.) **Plumbic Iodide** (PbI_2) [Molecular weight, 461 ; Sp. gr., 6·38].

Preparation.—By mixing solutions of plumbic acetate and potassic iodide.

Properties.—A bright yellow powder, almost insoluble in cold water, but soluble in hot, the solution on cooling depositing golden scales of the iodide. It dissolves in alkaline iodides to form double salts.

A blue compound of a lead oxy-iodide with a lead carbonate is known ($Pb_2OI_4,4PbCO_3$).

COMPOUNDS OF LEAD AND SULPHUR.

(12.)	Plumbous sulphide	Pb_2S.
(13.)	Plumbic sulphide	PbS.

(12.) Plumbous Sulphide.—*Subsulphide of lead* (Pb_2S). This compound is produced during the process of smelting galena. It may be prepared by heating PbS in a closed vessel, part of the sulphur being expelled.

(13.) Plumbic Sulphide.—*Protosulphide of lead; galena* (PbS) [Mol. wt., 239; Sp. gr., 7·59]. Found native as galena.

Preparation.—(1.) (*As a hydrate.*) By the action of sulphuretted hydrogen on a lead salt.

(2.) (*Anhydrous.*) By fusing sulphur with lead, or by passing sulphur vapor over metallic lead.

Properties.—The natural sulphide crystallizes in cubes, presenting a metallic appearance. The artificial sulphide formed by Process 1 is a black amorphous powder. If the sulphide be heated in the presence of air, a mixture of plumbic oxide and plumbic sulphate is formed, a part of the sulphur being expelled. Heated *in vacuo* it fuses at a bright red heat without decomposition, and may even be sublimed in a current of H or of CO_2, the sublimate presenting a crystalline appearance. Strong nitric acid converts it into a sulphate, dilute nitric acid changing it into a nitrate with the separation of sulphur. Boiling hydrochloric acid decomposes it, with the evolution of H_2S.

Various other sulphides, such as Pb_4S and PbS_5 have been obtained.

Various sulphochlorides are described, viz., ($PbCl_2,PbS$) and ($3PbS,PbCl_2$). They are produced when H_2S, insufficient for complete precipitation, is passed through acid solutions of lead chloride.

LEAD OXY-SALTS.

(19 to 22.) Plumbic Nitrate ($Pb2NO_3$). (Mol. wt., 331; Sp. gr., 4·4.)

Preparation.—By dissolving either the metal, its oxide or carbonate, in dilute nitric acid, and evaporating the solution to the crystallising point.

Properties.—A white, opaque, crystalline (octahedral) substance, soluble in water (1 in 8 at 60° F.), insoluble in alcohol, and decomposed by heat into PbO, O, and N_2O_4.

Uses.—As a mordant in dyeing and calico printing.

Several *basic plumbic nitrates*, such as ($Pb2NO_3,PbH_2O_2$), etc., and also several *plumbic nitrites*, are known.

(14.) Plumbic Sulphate ($\mathrm{PbSO_4}$) [Mol. wt., 303; Sp. gr., 6·3] is found native as "Anglesite," or "lead vitriol." It also occurs combined with lead carbonate as "Lanarkite."

Preparation.—(1.) By adding sulphuric acid, or a soluble sulphate, to a salt of lead in solution.

(2.) It occurs as a secondary product in the manufacture of aluminium acetate.

Properties.—A white powder, soluble in sodium thiosulphate, in ammonium acetate and tartrate, and in concentrated sulphuric acid. It is also slightly soluble in nitric and hydrochloric acids, but is practically insoluble in water (1 in 22,000 parts).

A *diplumbic sulphate* ($\mathrm{Pb_2SO_4}$), a *plumbic sulphite* ($\mathrm{PbSO_3}$), and a *plumbic dithionate* ($\mathrm{PbS_2O_6,4H_2O}$) are recorded. Certain double compounds such as [$\mathrm{(NH_4)_2SO_4,PbSO_4}$] are also said to exist.

(16.) Carbonate of Lead ($\mathrm{PbCO_3}$) [Sp. Gr., 6·46] is found native as "cerussite." *White lead,* or *ceruse,* is a basic carbonate (either $\mathrm{3PbCO_3,PbH_2O_2}$ or $\mathrm{2PbCO_3,PbH_2O_2}$).

Preparation of White Lead.—The principal reactions involved in its preparation are as follows:—

(1.) The formation of an *acetate of lead,* $\mathrm{Pb2(C_2H_3O_2)}$, by the action of acetic acid on oxide of lead.

(2.) From this acetate, a basic *acetate of lead* is then formed [$\mathrm{PbO, Pb2(C_2H_3O_2)}$].

(3.) By acting on this basic lead acetate with $\mathrm{CO_2}$, the lead oxide is converted into carbonate, whilst the normal acetate of lead remaining is again capable of combining with more oxide. Thus—

$$\mathrm{PbO,Pb2(C_2H_3O_2)} \quad + \quad \mathrm{CO_2} \quad = \quad \mathrm{PbCO_3} \quad + \quad \mathrm{Pb2(C_2H_3O_2)}$$

Basic acetate of lead + Carbonic anhydride = Plumbic carbonate + Normal acetate of lead.

Processes adopted in the Preparation of White Lead:—

(A.) *Dutch Process.*—A piece of lead is placed in a glazed earthen pot containing weak crude vinegar. A large number of these pots, built up in heaps, are imbedded in spent tan or horse dung, an arrangement for the supply of air being made by means of gratings. The heat volatilises the vinegar (acetic acid), which, with air, converts the surface of the lead into a basic plumbic acetate:—

$$\mathrm{2C_2H_4O_2} \quad + \quad \mathrm{2Pb} \quad + \quad \mathrm{O_2} \quad = \quad \mathrm{PbO,Pb2(C_2H_3O_2),H_2O.}$$

Acetic acid + Lead + Oxygen = Basic lead acetate.

The $\mathrm{CO_2}$ set free by the tan acts on this basic acetate, forming water, the normal acetate, and white lead or the basic carbonate:—

$$\mathrm{3[PbO,Pb2(C_2H_3O_2)H_2O]} \quad + \quad \mathrm{2CO_2} \quad = \quad \mathrm{2H_2O} \quad + \quad \mathrm{3Pb2(C_2H_3O_2)}$$

Basic lead acetate + Carbonic anhydride = Water + Normal lead acetate

$$+ \quad \mathrm{2PbCO_3,PbO,H_2O.}$$

+ Basic lead carbonate.

The normal acetate thus formed in the presence of water and oxygen reacts on a fresh portion of lead :—

$$\begin{array}{ccccccccc} Pb2(C_2H_3O_2) & + & Pb & + & O & + & H_2O & = & PbO,Pb2(C_2H_3O_2)H_2O, \\ \text{Normal lead acetate} & + & \text{Lead} & + & \text{Oxygen} & + & \text{Water} & = & \text{Basic lead acetate,} \end{array}$$

This basic lead acetate, if again acted on by carbonic acid, is converted into the basic carbonate. Thus, after some weeks, the lead is almost entirely changed into carbonate. The weak vinegar supplies the water and the acetic acid, and the putrefying organic matter (the tan or dung, whichever be used) the carbonic anhydride and the necessary warmth to volatilize the acetic acid. 100lbs. of acetic acid serves to convert 50 tons of lead into white lead. The carbonate thus prepared (but which always contains more or less lead oxide) is then ground and levigated, an operation which in the case of the dry material, acts very deleteriously on the workpeople.

(B.) *Thénard's Process.*—This consists in first boiling together litharge and acetic acid, and afterwards decomposing the tribasic acetate formed with a current of carbonic anhydride. The product is said to be inferior as a pigment to that prepared by the Dutch process.

(C.) *Milner's Process.*—A mixture of caustic soda and lead oxychloride is formed by grinding together litharge, common salt, and water. Carbonic anhydride is passed into this mixture until it exhibits a neutral reaction.

Properties.—Lead carbonate is practically insoluble in water (1 in 50,000), unless the water be charged with carbonic acid. Heat decomposes it into CO_2 and PbO. Acids dissolve it, with effervescence.

In common with all lead salts, lead carbonate is blackened by a mere trace of sulphuretted hydrogen. The blackening, however, disappears on prolonged exposure to light and air, the black plumbic sulphide becoming converted into white plumbic sulphate.

Plumbic phosphates (p. 165), arsenate, chromate (p. 416), and borate are also known. No definite silicate has been described.

REACTIONS OF LEAD COMPOUNDS.

Excepting the nitrate and acetate, lead salts are almost insoluble in water.

In solution :—

(1.) *Hydrochloric acid;* a white ppt. ($PbCl_2$), soluble in boiling water.
(2.) *Dilute sulphuric acid;* a white ppt. ($PbSO_4$).
(3.) *Caustic alkalies;* a white ppt. (PbH_2O_2), soluble in excess.
(4.) *Alkaline carbonates* ; a white ppt. ($PbCO_3$).
(5.) *Potassium iodide* ; a yellow ppt. (PbI_2).
(6.) *Potassium chromate;* a yellow ppt. ($PbCrO_4$).
(7.) *Ammonium sulphide* or *sulphuretted hydrogen ;* a black ppt. (PbS).

[NOTE.—If a large quantity of HCl be added to the solution, a yellowish precipitate may present itself for a few seconds after the passage of the sulphuretted hydrogen has been started. This probably consists of some variety of sulphide in combination with a chloride (*a chlorosulphide*) $PbCl_2,3PbS$ (?).]

8. *Blowpipe on charcoal.* A malleable globule (which marks paper), together with a yellow incrustation of oxide.

SILVER (*Argentum*) (Ag).

Atomic weight, 108. *Molecular weight* (*probable*), 216. *Specific heat*, 0·056. *Specific gravity*, 10·57. *Fuses at* 1904° F. (1040° C.) *Atomicity, monad* ($AgCl$; Ag_2O).

History.—Silver was known to the ancients (☽ = Luna).

Natural History.—Silver is found in a free state. It also occurs as a *sulphide*, "silver glance" (Ag_2S); as a *chloride* (kerargyrite, "horn-silver") ($AgCl$); and as a *carbonate*. Also as a compound of *bromide* and *chloride* ("embolite") ($2AgBr,3AgCl$); and as a *sulphantimonite* (pyrargyrite, "dark-red silver ore") (Ag_3SbS_3). It is present in small quantities (2 or 3 ozs. per ton) in galena (PbS). A minute trace occurs in sea-water and in some sea-weeds. The burnt pyrites used in the manufacture of sulphuric acid often contains about $\frac{1}{2}$ oz. of silver to the ton.

Extraction.—(1.) *Cupellation Process of Pattinson.*—From argentiferous lead (*see* p. 521).

(2.) *Amalgamation Process.*—The powdered ore (generally a sulphide) is first roasted with sodium chloride, whereby a silver chloride is formed. The mass is then agitated in revolving casks with water into which mercury and scraps of iron have been placed. The iron reduces the silver to the metallic state, whilst the mercury dissolves the reduced silver ($Fe+2AgCl = FeCl_2+Ag_2$). The amalgam thus formed is then distilled, when the mercury passes over, leaving the silver in the retort.

In this process a film of mercuric sulphide separates the globules of mercury, and renders them liable to be lost in washing (flouring or sickening). To remedy this about 2 per cent. of sodium is added to the mercury, in order that sodium sulphide may be formed.

In Mexico the finely-powdered ore, made into a mud with water, is mixed with common salt, to which are added about 1 per cent. of *magistral* (mixed iron and copper sulphates obtained by roasting copper pyrites) and a quantity of mercury. After about six weeks' incorporation (commonly effected by the treading of mules), the amalgam is separated by washing, and is then distilled.

Wet Processes.—(1.) (Ziervogel's.) Argentiferous copper pyrites is first heated at a regulated temperature, so as to decompose the sulphates of iron and copper formed, the argentic sulphate remaining undecomposed. The mass thus formed is lixiviated with boiling water, and the silver precipitated from the solution by metallic copper.

(2.) (Von Patera's.) By first roasting the ore with sodic chloride and afterwards dissolving out the AgCl with sodic thiosulphate. From this solution the silver may be precipitated with sodic sulphide, the argentic sulphide formed being reduced by heat in a current of air.

Preparation of pure Silver.—Dissolve the impure metal in nitric acid. Precipitate the silver as AgCl, with hydrochloric acid. Collect, wash, dry, and fuse the precipitated chloride with anhydrous sodic carbonate in an earthen crucible.

Properties.—(α.) *Physical.* A white metal, with high lustre, very malleable and ductile, and the best conductor of heat and electricity known. It may be crystallized (regular octahedra). Sp. gr. 10·57. It is harder than gold, but not so hard as copper. Very thin leaves are said to transmit a bluish-green light.

It fuses at 1904° F. (1040° C.), expanding greatly on cooling at the moment of solidification. Distils at a white heat.

(β.) *Chemical.* Silver is unacted upon at any temperature either by moisture or by air (Ozone probably oxidizes it). When melted, however, in air, it absorbs mechanically more than 22 times its bulk of oxygen, disengaging it again on solidification. (This accounts for what is known as the "*spitting*" of the globule.) This absorption of oxygen may be prevented by the admixture of 1 or 2 per cent. of copper with the silver.

Action of Acids.—Hot sulphuric and dilute nitric acids dissolve silver. With the former, Ag_2SO_4 is formed, and sulphurous anhydride (SO_2) evolved; and with the latter, $AgNO_3$ is formed, and nitric oxide (NO) evolved. Hydrochloric acid is decomposed by red-hot silver, hydrogen and argentic chloride being formed. Strong aqueous hydriodic acid dissolves it, evolving hydrogen and depositing crystals of (AgI,HI), which ultimately, on exposure to air, yield argentic iodide (AgI).

Silver is unaffected by the alkalies; hence in the laboratory silver vessels can be used where platinum and glass are inadmissible. It combines with the haloids. If NaCl be fused in, or even kept for a lengthened period in contact with a silver dish, AgCl and NaHO will be formed. The metal when fused unites with phosphorus. Exposed to air, it rapidly blackens, Ag_2S being formed by the action upon it of the sulphuretted hydrogen present in the atmosphere. Pure H_2S, however, has no action upon silver.

Uses.—For coinage and plate (925Ag and 75Cu = 1000 English standard silver). "*Frosted silver*" is produced by heating silver in air, and then immersing it in dilute sulphuric acid. "*Oxidized silver*" is produced by dipping the metal in the solution obtained on boiling together sulphur and potash, whereby the silver becomes covered with a very thin film of sulphide. Electro-plating is performed by depositing silver on some baser metal by electrical agency. The article to be silvered is made the negative, and a plate of silver the positive electrode, a solution of argentic cyanide in an excess of potassic cyanide being the liquid (electrolyte) employed. The strength of the solution is maintained and rendered constant by the cyanogen, liberated at the positive electrode, combining with the silver of which the positive electrode is composed.

In silvering mirrors, the surface of the plate to be silvered is first immersed in a solution containing milk-sugar (or other organic reducing agent) and then in an ammoniacal solution of silver. A bright silver film is thus deposited on the glass. In ordinary mirrors this silver film is deposited on the back of the glass, whilst in telescopic mirrors the deposit is thrown down on the front surface, thus avoiding the passage of the light before reflection through the substance of the glass itself.

Compounds of Silver (Ag = 108).

	COMPOUNDS.		Formulæ (Common).	Molecular Weight.	Specific Gravity.	Ag per cent.
1	Oxides.	Argentous oxide	Ag_4O	448·0		
2		Argentic oxide	Ag_2O	232·0	7·2	93·1
3		,, peroxide	Ag_2O_2	248·0	5·47	
4	Chlorides.	Argentous chloride	Ag_2Cl			
5		Argentic chloride	$AgCl$	143·5	5·55	75·26
6		,, bromide	$AgBr$	188·0	6·35	57·45
7		,, iodide	AgI	235·0	5·5	45·96
8		,, fluoride	AgF	127·0		
9		,, cyanide	$AgCy$	134·0		
10		,, sulphide	Ag_2S	248·0	7·2	87·1
11		,, sulphate	Ag_2SO_4	312·0	5·32	
12		,, hyposulphate	$Ag_2S_2O_6$ (?)			
13		,, thiosulphate	$Ag_2S_2O_3$			
14		,, dithionate	$Ag_2S_2O_6.H_2O$			
15		,, sodic thiosulphate	$NaAgS_2O_32H_2O$			
16		,, sulphite	$AgSO_2$			
17		,, arsenate	$AgAsO_4$			
18		,, nitrate	$AgNO_3$	170·0	4·33	
19		,, nitrite	$AgNO_2$	154·0		
20		,, chlorate	$AgClO_3$			
21		,, bromate	$AgBrO_3$			
22		,, iodate	$AgIO_3$			
23		,, periodate	$AgIO_4$			
24		,, arsenite	$AgAsO_3$			
25		,, sulpharsenite	$AgAsS_3$			
26		,, sulphantimonite	$AgSbS_3$			
27		,, carbonate	Ag_2CO_3	276·0		
28	Phosphates.	,, phosphate	Ag_3PO_4	419·0	7·32	
29		,, pyrophosphate	$Ag_4P_2O_7$		5·30	
30		,, metaphosphosphate	$AgPO_3$			

COMPOUNDS OF SILVER AND OXYGEN.

1. Argentous oxide ... ... Ag_4O.
2. Argentic oxide ... ... Ag_2O.
3. Argentic peroxide ... ... Ag_2O_2.

(1.) Argentous Oxide; *Suboxide* and *Quadrantoxide of Silver* (Ag_4O).

Preparation.—By heating argentic citrate to 212° F. (100° C.) in a current of hydrogen. The residue, which contains argentous citrate, is then dissolved in water, and the argentous oxide precipitated from the solution by potassic hydrate.

Properties.—A black powder, easily decomposed by heat and by oxy-acids, a silver salt of the acid being formed and metallic silver set free. It is soluble in ammonia. It is also soluble in hydrogen acids, the corresponding haloid or other compound being formed.

(2.) Argentic Oxide; *Protoxide* or *Monoxide of Silver* (Ag_2O).

Preparation.—(1.) By heating to 140° F. (60° C.), the brown hydrated oxide ($AgHO$) (produced when potassic hydrate is added to a solution of a silver salt).

(2.) By boiling freshly precipitated silver chloride in a strong solution of caustic potash.

Properties.—(*a.*) *Physical.* A brown substance, completely decomposed at 482° F. (250° C.), and partially decomposed by sunlight. Sp. gr. 7·2.

(*β.*) *Chemical.* Dry argentic oxide is a powerful oxidising agent, inflaming sulphur, phosphorus, etc., when mixed with them. It is also a powerful base, the salts formed being isomorphous with the alkaline salts. Its solution in water (1 part in 3,000 of water) is feebly alkaline. It is insoluble in solutions of sodic or of potassic hydrates. The freshly precipitated oxide dissolves readily in ammonia, the solution slowly depositing crystals of the explosive compound known as "*fulminating silver*" (NH_2Ag ?). The oxide forms a yellow glass with the fusible silicates.

(3.) Argentic Peroxide; *Silver dioxide* (Ag_2O_2).

This energetic oxidising agent is formed by the action of ozone on finely divided silver. It is deposited in small grey crystals (octahedra) on the positive pole, when a voltaic current is passed through a solution of argentic nitrate. It is decomposed at 212° F. (100° C.). When acted upon by chlorine, or by nitric and sulphuric acids, oxygen is set free, corresponding silver compounds being formed. From hydrochloric acid, it liberates chlorine. It is a powerful oxidizer, firing H_2S—undergoing reduction when heated in hydrogen, etc. It both decomposes, and is decomposed by ammonia, nitrogen being evolved. Mutual reduction occurs when silver peroxide is acted upon with peroxide of hydrogen ($2Ag_2O_2 + 2H_2O_2 = 2Ag_2 + 2H_2O + 3O_2$).

COMPOUNDS OF SILVER AND CHLORINE.

4. Argentous chloride	Ag_2Cl.
5. Argentic chloride	$AgCl$.

(4.) Argentous Chloride; *Subchloride of silver* (Ag_2Cl).

Preparation.—(1.) By precipitating a solution of argentous citrate with sodium chloride.

(2.) By the action of ferric chloride on metallic silver ($2Ag_2 + Fe_2Cl_6 = 2Ag_2Cl + 2FeCl_2$).

(3.) By the action of hydrochloric acid on argentous oxide.

Properties.—A black substance insoluble in nitric acid. By the action upon argentous chloride of heat, or of ammonia, or of nitric acid, it is converted into argentic chloride, silver being set free.

(5.) Argentic Chloride ($AgCl$).—[*Mol. Wt.*, 143·5 ; *Sp. Gr.*, 5·5.]

Natural History.—Silver chloride is found native both in cubical crystals and as a compact semi-transparent mass called "horn-silver" (kerargyrite). It is found associated with argentic bromide in "embolite."

Preparation.—By adding hydrochloric acid, or a soluble chloride, to a soluble silver salt.

Properties.—A white substance, becoming violet on exposure to light, Ag_2Cl and a minute trace of free chlorine being formed. This change of color is not well understood. The decomposition is slow if the chloride be very pure, but more rapid if organic matter be present. Sp. gr., 5·5. It melts at 500° F. (260° C.) becoming a clear yellow liquid, which solidifies to a horny mass on cooling. It is slightly volatile, but does not decompose at a high temperature. It is insoluble in nitric acid, but is soluble in boiling concentrated hydrochloric acid (1 in 200), from which solution it may be precipitated by dilution with water. It is also soluble in solutions of the alkaline and earthy chlorides, forming with them double salts. Ammonia dissolves it freely, depositing crystals of the chloride on evaporation. Cold solutions of potassic or sodic hydrates do not act upon it, but when concentrated alkaline solutions are boiled with argentic chloride, an alkaline chloride is formed, and argentic oxide precipitated. The oxide is reduced when heated with glucose. The dry chloride absorbs ammonia, forming the compound $2AgCl,3NH_3$. This body evolves the ammonia at 100·4° F. (38° C.). The chloride is soluble in solutions of the thiosulphates, also in solutions of the soluble sulphites and chlorides, in a saturated solution of mercuric nitrate, and a solution of potassic cyanide. When digested in a solution of potassic bromide or iodide, argentic bromide or iodide are formed, potassic chloride remaining in solution. Hydrobromic acid at ordinary temperatures converts silver chloride into a bromide, hydriodic acid converting both the chloride and bromide into an iodide; but at 1292° F. (700° C.) hydrochloric acid gas converts both bromide and iodide of silver into the chloride. Silver chloride is not reduced when heated with carbon; but it is reduced either:—(1.) When heated in a current of hydrogen ($2AgCl + H_2 = Ag_2 + 2HCl$); or, (2,) when ignited with an alkaline carbonate ($4AgCl + 2Na_2CO_3 = 4NaCl + 2CO_2 + O_2 + 2Ag_2$); or, (3,) when brought into contact with easily oxidizable metals (*e.g.*, Zn, Fe, etc.).

Argentic chloride is largely used in photography.

(6 and 7.) **Argentic Bromide** ($AgBr = 188$) and **Argentic Iodide** ($AgI = 235$). Both compounds are found native.

Preparation.—By adding potassic bromide, or potassic iodide, to a solution of argentic nitrate.

Properties.—Both salts have a yellow color. They are insoluble in acids. The bromide is somewhat insoluble, and the iodide almost completely insoluble in ammonia, but both bromide and iodide are freely soluble in a solution of sodium thiosulphate.

The iodide fuses at a red heat. The Sp. gr. of the crystallized iodide is 5·5, and of the precipitated iodide, 5·8. It is said that between $-10°$ and $+70°$ C., the iodide contracts by heat and expands on the application of cold (Fizeau).

Argentic iodide is soluble in a strong solution of potassic iodide, depositing crystals of AgI,HI. It also dissolves in a boiling solution of argentic nitrate, depositing crystals of ($AgI,AgNO_3$) which are more sensitive to light than the simple iodide. It would appear, however, that the property of blackening on exposure to light does not occur with the pure iodide, but is dependent on the presence of foreign substances capable of combining with the liberated iodine. Its use in photography depends on the circumstance that a slight exposure to light renders the compound specially active, so that if in that condition it be acted upon with a silver salt and some reducing substance (like pyrogallic acid), finely divided silver is precipitated upon its surface (developing).

The dry iodide absorbs ammonia, forming ($2AgI,NH_3$). The dry bromide does not act in the same manner as the iodide in this respect, although it forms a compound with ammonia when in solution. The ammonia being disengaged from the iodide compound by heat, this body may be conveniently employed for preparing liquid ammonia in a Faraday tube.

Bromide and chloride of silver are converted into the iodide by hydriodic acid or by an aqueous solution of an iodide, the dry bromide or iodide undergoing conversion into the chloride by the action of chlorine or of hydrochloric acid gas at a temperature above 1292° F. (700° C.).

(8.) **Argentic Fluoride** ($AgF = 127$) is prepared by dissolving silver oxide or carbonate in hydrofluoric acid. When fused it conducts electricity, and is not, therefore, decomposed by an electric current. The dry fluoride absorbs more than 800 times its volume of ammonia.

COMPOUND OF SILVER AND SULPHUR.

(9.) Argentic Sulphide (Ag_2S). [*Mol. Wt.*, 248; *Sp. Gr.*, 7·2.]

Natural History.—The sulphide is found native, both in a massive and crystalline form as "silver glance" (argentite). It also occurs combined with the sulphides of antimony and arsenic as "dark" and "light-red silver ores."

Preparation.—(1.) By passing sulphuretted hydrogen through a solution of a salt of silver, or by allowing the gas to come into contact with metallic silver.

(2.) By heating the metal with sulphur in a covered crucible.

Properties.—(α.) *Physical.* It is a soft, dark-colored, fusible body, conducting electricity when hot, but not when cold. It fuses by heat if air be excluded, but in the presence of air a silver sulphate is first formed which is itself decomposed when more strongly heated. It is insoluble in water.

(β.) *Chemical.* Boiling sulphuric acid forms with it argentic sulphate, sulphurous anhydride being set free. Boiling hydrochloric acid forms argentic chloride, sulphuretted hydrogen being set free. Nitric acid forms with it a yellow body, having the formula ($Ag_2S,AgNO_3$). The alkalies decompose it on the application of heat. It is not soluble in solutions of the alkaline sulphides. It is decomposed by cupric chloride (argentic chloride being formed); also by ignition with many of the metals, such as Cu, Pb, Fe, etc.

OXY-SALTS OF SILVER.

(10.) Argentic Sulphate (Ag_2SO_4). [*Mol. Wt.*, 312; *Sp. Gr.*, 5·32.]

Preparation.—(1.) By boiling together silver and sulphuric acid. The salt may be precipitated from this solution by the addition of water.

(2.) By precipitating a strong solution of the nitrate with sulphuric acid.

Properties.—A crystalline body, somewhat insoluble in water (1 in 200 aq. at 60° F.; 1 in 88 aq. at 212° F.). Fuses at a red heat without decomposition, but at a higher temperature breaks up into silver, oxygen, sulphurous and sulphuric anhydrides.

An acid silver sulphate ($AgHSO_4$) has been prepared.

(11.) Argentic Nitrate.—*Nitrate of silver; lunar caustic* ($AgNO_3$). [*Molecular weight*, 170; *Sp. Gr.*, 4·33.]

Preparation.—By dissolving the metal in nitric acid, and either crystallising or evaporating the solution to dryness.

Properties.—A colorless crystalline salt (tabular rhombs). The pure salt is unacted upon by light, but is blackened in the presence of organic matter. It is soluble in water, the solution being neutral (1 in 1 at 60° F.; 2 in 1 at 212° F.). It is also soluble in boiling alcohol (1 in 4). It is insoluble in nitric acid. A concentrated solution of the nitrate absorbs ammonia ($AgNO_3,2NH_3$) and dissolves the haloid silver salts, forming various compounds (as ($AgNO_3,AgCl$)) which are decomposed on the addition of an excess of water. It fuses at 392° F. (200° C.), the solidified nitrate, when cast into sticks, forming what is called "lunar caustic." At higher temperatures the salt undergoes decomposition.

Silver nitrate is used in surgery as an escharotic. Its action depends on the readiness with which it parts with its oxygen, the oxygen combining with the organic matter and the silver being precipitated. The pure salt undergoes no alteration by exposure to light, the change of color usually observed depending on the presence of organic bodies. To this is due the blackening of the skin when "lunar caustic" is applied to it. Thus the salt is used in photography, for hair-dyes, for indelible marking inks, etc. In the case of marking inks, either the fabric is first mordanted with sodic carbonate, and then written upon with an argentic nitrate solution, whereby an argentic carbonate is precipitated (a salt easily blackened), or the fabric is written upon without preparation with a solution of argentic nitrate containing an excess of ammonia, which combines with the nitric acid of the silver salt.

REACTIONS OF SILVER SALTS.

Spectrum.—No flame spectrum. Spark spectrum gives two bright lines in the green.

Caustic alkalies or *ammonia.*—A brown ppt. of Ag_2O. (In the case of ammonia, the precipitate is soluble in excess.)

Sulphuretted hydrogen.—A black ppt. of Ag_2S; soluble in hot HNO_3; insoluble in ammonium sulphide.

Hydrochloric acid or a *Soluble chloride.*—Ppt. of AgCl; freely soluble in ammonia.

Hydracids.—Ppt. of the haloid or allied compound.

Hydrocyanic acid and *Potassic cyanide.*—Ppt. of AgCy, soluble in excess of KCy. [If the AgCy be ignited, metallic silver only remains in the deposit.]

Sulphurous acid; Ferrous sulphate, etc.; *Oxidizable metals* (as Cu, etc.).—Ppt. of metallic silver from solutions of silver salts.

Blowpipe.—The insoluble silver compounds heated on charcoal with sodium carbonate leave metallic silver.

MERCURY (Quicksilver) ($Hg = 200$).

Atomic and molecular weight 200 (p. 39). *Molecular and atomic volume,* $\boxed{|}$. *Specific gravity of solid metal at* – 37·9° F. (–38·8° C.), 14·0; *of liquid metal at* 60° F. (15·5° C.), 13·56; *of vapor*, 6·97. *Fuses at* – 37·9° F. (– 38·8° C.) *Boils at* 675° F. (357·2° C.). *Specific heat,* 0·0319. *Atomicity; dyad in mercuric compounds* ($Hg''Cl_2$), *and pseudo-monad in mercurous compounds* ($'Hg'Hg'Cl_2$).

History.—Known to the ancients (*hydrargyrum; argentum vivum*).

Natural History.—It is found native, but occurs chiefly as a *sulphide*, "cinnabar" (HgS). It is also found as a *chloride* (calomel) (Hg_2Cl_2) and as an *iodide;* also as an amalgam with gold and silver.

Extraction.—(1.) *Process adopted at Almaden, in Spain.* The ore (HgS) is roasted in a current of air, and the mercury condensed either in stone chambers or stoneware bottles (aludels). Any metallic vapours that escape are afterwards recovered by passing them through a tower into which a shower of water plays. The sulphurous acid, evolved during the process, is allowed to escape into the air.

(2.) *Process adopted in the Palatinate.*—The ore (HgS) is distilled with lime. The mercury is collected as it passes over, the sulphur remaining in the retort in the form of calcium sulphide and sulphate ($4HgS + 4CaO = 3CaS + CaSO_4 + 2Hg_2$). (Scraps of iron (smithy-scales) may be used instead of lime, when ferrous sulphide would remain in the retort.)

Impurities.—Chiefly tin and lead. The metal is first filtered through linen to free it from earthy matters, and afterwards purified by distillation. Agitating the metal with dilute nitric acid is also an effectual method of effecting further purification.

Properties.—(*a.*) *Physical.* Mercury is a silvery-white, lustrous, liquid metal. It is the only metal liquid at ordinary temperatures. When pure it is perfectly mobile, and non-adherent to glass;—in other words, it runs over an inclined surface without leaving any tail or track of oxide behind. It becomes solid at – 37·9° F. (– 38·8° C.). contracting greatly on solidification. The solid mercury has a specific gravity of 14·0. It crystallizes in octahedra, and is very malleable. Above 41° F. (5° C.) mercury is slightly volatile. If a thin layer, such as the film of a bubble of the metal, be examined, it will be found to transmit a blue light. The vapor of mercury (Sp. gr., 6·97) is transparent, conducting neither heat nor electricity. At 675° F. (357° C.) the metal boils.

[Note.—The vapor density of mercury compared with air is 6·7, and as compared with hydrogen 100;—that is, its vapor density is one-half its atomic weight. Hence the mercury atom (like the cadmium atom) occupies in the state of gas twice the volume occupied by the hydrogen atom.—Page 39.]

(β.) *Chemical.* Mercury is not tarnished (if pure) either by air or water at ordinary temperatures, although it appears that, when reduced to a minute state of subdivision, *e.g.*, by trituration with various substances chemically inert upon it, such as chalk or grease [as in the preparation of the hyd. c. cret., and pil. hydrargyri, etc., of the Pharmacopœia], the metal undergoes a partial oxidation (Hg_2O), to which the active properties of these medicines are probably due. This circumstance accounts for the varying medicinal qualities of "Grey powder," which at one time may act as a mild laxative, and at another as an active poison. Mercury undergoes rapid oxidation in the presence of ozone. It freely absorbs oxygen when heated to 800° F. (426° C.), becoming the red oxide (HgO). At a dull red heat this oxide is decomposed into mercury and oxygen. Neither hot or cold hydrochloric acid, nor cold sulphuric acid have any action upon it. When the metal is heated with sulphuric acid, sulphurous anhydride is evolved and a mercurous sulphate formed if the metal be present in excess and the heat employed be not too great, a mercuric sulphate being produced if an excess of acid over the metal be added. With strong nitric acid, a mercuric nitrate is formed, nitric oxide being evolved. By the action of dilute nitric acid upon the metal a mercurous nitrate results, a basic mercurous nitrate being formed if the mercury be in excess.

The metal combines at common temperatures with sulphur, with the haloids, and also with many of the metals, forming with them compounds of definite composition. Iron and platinum are the only metals not corroded by mercury.

AMALGAMS.

An amalgam is an alloy containing mercury.

Preparation of amalgams.—(1.) By the direct union of mercury with other metals, with or without the application of heat (*Examples*, Au, Ag, Sn, Na, K).

(2.) By the electrolysis of a metallic solution, using mercury as the negative electrode (*Example*, NH_4).

(3.) By the action of sodium amalgam on a metallic salt or on a metal (*Example*, Fe).

(4.) By the immersion of a metal in the solution of a mercury salt (*Example*, Cu).

Properties.—In some cases the combination of a metal with mercury occurs with the evolution of heat (Na ; K), whilst in other cases an absorption of heat (cold) results (Sn). Amalgams exist in various states. The amalgam of 1K and 96Hg is solid, whilst that of 1K and 140Hg is liquid. A 30 per cent. copper amalgam is very hard at ordinary temperatures, whilst at 212° F. (100° C.) it becomes plastic, recovering its hardness as the temperature is lowered. Thus a copper amalgam is used in dentistry for stopping teeth, its advantage for this purpose being that the specific gravity both of the hard and of the plastic variety is identical.

When sodium and potassium amalgams are acted on by water, hydrogen is evolved. Hence the use of sodium amalgam as a reducing agent. A tin amalgam is used for silvering mirrors. The formation of a silver and of a gold amalgam is taken advantage of in the extraction of these metals from their ores (*q. v.*).

Uses of Mercury.—In medicine, as blue pill, grey powder, etc. The physiological action of the pure liquid metal is practically *nil*, but many mercury compounds are active poisons. Workmen exposed to the action of mercury vapor, become affected with mercurial palsy. Mercury is also used as an amalgam with tin for silvering looking-glasses; also for amalgamating zinc plates; also for the extraction of gold and silver from their ores, depending on the readiness with which it forms an amalgam with these metals; also for barometers, thermometers, etc.

COMPOUNDS OF MERCURY.

These are of two kinds :—

(1.) *Mercuric compounds;* where the molecule contains one atom of dyad mercury ($\mathrm{Hg''O}$).

(2.) *Mercurous compounds;* where the molecule contains two atoms of mercury, which together act as a dyad (*pseudo-monad*) ($\mathrm{Hg_2O}$).

Compounds of Mercury (Hg = 200).

		COMPOUNDS.	Formulæ (General).	Molecular Weight.	Specific Gravity.	Hg per cent.
1	Oxides.	Mercurous oxide (black oxide)	$\mathrm{Hg_2O}$	416	10·68	96·15
2		Mercuric oxide (red oxide)	HgO	216	11·29	92·59
3	Chlorides.	Mercurous chloride (calomel)	$\mathrm{Hg_2Cl_2}$	471	7·14	84·92
4		Mercuric chloride (corrosive sublimate) ..	$\mathrm{HgCl_2}$	271	5·42	73·80
		[Bromides, iodides, and fluorides analogous to chlorides.]				
5		Mercuric ammonium chloride (white precipitate)	$\mathrm{NH_2Hg''Cl}$			
6		Mercurous iodide (green)	$\mathrm{Hg_2I_2}$	654		
7		Mercuric iodide (red)	$\mathrm{HgI_2}$	454	6·25	44·05
8	Sulphides.	Mercurous sulphide (Ethiop's mineral) ..	$\mathrm{Hg_2S}$	232	6·28	
9		Mercuric sulphide (vermilion or cinnabar)	$\mathrm{HgS''}$	232	8·2	86·21

	COMPOUNDS.	Formulæ (General).	Molecular Weight.	Specific Gravity.	Hg per cent.
10	Mercuric nitride ..	Hg_3N_2			
11	Mercurous sulphate ..	Hg_2SO_4	496		
12	Mercuric sulphate ..	$HgSO_4,H_2O$	296 + 18	6·46	
13	Basic-mercuric sulphate (Turpeth mineral)	$HgSO_4,2HgO$		8·319	
14	Mercurous nitrates	$Hg_22NO_3,2H_2O$ Hg_2HNO_4	524 + 36		
15	Mercuric nitrates..	$Hg2NO_3,8H_2O$ $Hg2NO_3,HgO,2H_2O$			
16	,, phosphate ..	$Hg_3P_2O_8$			
17	Mercurous chlorate ..	$HgClO_3$			
18	,, perchlorate	$HgClO_4,3H_2O$			
19	,, bromate ..	$HgBrO_3$			
20	,, carbonate	Hg_2CO_3			
21	Mercuric carbonates	$4HgO,CO_2$ $3HgO,CO_2$			

COMPOUNDS OF MERCURY AND OXYGEN.

1. Mercurous oxide (black oxide) ... Hg_2O.
2. Mercuric oxide (red oxide) ... ... HgO.

(1.) **Mercurous Oxide.**—*Suboxide*, *black* or *grey oxide of mercury* Hg_2O). [*Molecular weight*, 416. *Specific gravity*, 10·68.]

Preparation.—By decomposing a mercurous compound (*e.g.* calomel) ith potassic hydrate ($Hg_2Cl_2 + K_2O = Hg_2O + 2KCl$).

Properties.—A powerful base. It undergoes rapid decomposition a heat of 212° F. (100° C.), decomposing slowly even by exposure light ($2Hg_2O = 2HgO + Hg_2$). Soluble in acids, forming mercurous lts.

The efficacy of blue pill, grey powder, etc., is believed to be due to e presence of this oxide.

(2.) **Mercuric Oxide.**—*Mercury monoxide*; *Red oxide* or *Nitric* (or *tro-*) *oxide of mercury*; *Red precipitate* (HgO). [*Molecular weight*, 216.]

Preparation.—(1.) By heating mercury to 800° F. (426° C.) in air.

(2.) By gently heating a mixture of equal parts of mercury and ercuric nitrate until red fumes cease to be evolved. [Hence the name *tric oxide of mercury.*]

(The two varieties formed as above are red and crystalline.)

(3.) By mixing a solution of sodium hydrate with a solution of a ercuric salt.

(This variety is amorphous, and of a yellow color.)

Properties.—(*a.*) *Physical.* The oxide is black when hot, and either d and crystalline or yellow and amorphous when cold. The yellow ariety has the more active chemical affinities. Sp. gr., 11·2. The oxide is decomposed at a dull red heat ($HgO = Hg + O$). It is slightly soluble in water, the solution having an alkaline reaction and a metallic taste.

(β.) *Chemical.* The red and yellow varieties appear to be allotropic modifications of the same salt:—

(1.) The *yellow* variety is converted by a cold solution of oxalic acid, into an oxalate. It is rapidly changed into an oxy-chloride when boiled with a solution of mercuric chloride, and into a basic mercuric chromate ($HgCrO_4,2HgO$) when boiled with a solution of potassium bichromate.

(2.) The *red* variety is not acted upon by oxalic acid. It is very slowly acted upon by a mercuric chloride solution, and when boiled with a solution of potassium bichromate forms the compound $HgCrO_4,3HgO$.

It is soluble in fused potassic or sodic hydrate, from which solution a crystalline body may be obtained (K_2O,HgO).

By the action of concentrated ammonia upon mercuric oxide, the compound $Hg_4N_2H_2O_2,4H_2O$ (tetra-mercur-ammonic hydrate) is formed. This body, which was first examined by Mellon, is a yellowish substance, easily decomposed by friction, or even by exposure to light. Chemically, it possesses strong basic properties. Heated to 260° F. (126·1° C.), it becomes *mercuramine* ($Hg_4N_2H_2O_2,H_2O$), a dark brown substance, insoluble both in water and alcohol.

By passing ammonia gas over the yellow oxide, and then cautiously heating the residue to 260° F. (126·1° C.), the brown explosive *nitride of mercury* ($N_2Hg''_3$) is formed (see p. 310). By the action of acids, this body yields salts both of mercury and ammonium. It may be regarded as a double ammonia molecule, where six atoms of hydrogen are displaced by three atoms of divalent mercury.

Compounds of Mercury and Chlorine.

3. Mercurous chloride ... ... Hg_2Cl_2.
4. Mercuric chloride ... ... $HgCl_2$.

---

5. Mercur-ammonic chloride ... ... $NH_2Hg''Cl$.

(3.) Mercurous Chloride.—*Subchloride* or *Protochloride of mercury*; *Calomel* (Hg_2Cl_2). [*Molecular weight*, 471. *Specific gravity, solid*, 7·14; *of vapour*, 8·14.]

Natural History.—Occurs in a crystalline form as *horn-quicksilver.*

Preparation.—(1.) By precipitating a solution of mercurous nitrate with hydrochloric acid or with a soluble chloride.

(2.) (*Usual Process.*) By subliming a mixture of corrosive sublimate (17 parts) and mercury (13 parts) ($HgCl_2 + Hg = Hg_2Cl_2$). [The heat is ordinarily applied in cast-iron receivers, and the calomel formed condensed in brick chambers. The product requires thorough washing to remove any $HgCl_2$.]

(3.) By well triturating together mercuric sulphate (2 parts), mercury (4 parts), and sodic chloride (3 parts), and subsequently subliming the mixture ($HgSO_4 + Hg + 2NaCl = Hg_2Cl_2 + Na_2SO_4$).

(4.) By passing sulphurous anhydride through a saturated aqueous solution of crystalline mercuric chloride heated to 122° F. (50° C.) ($2HgCl_2 + 2H_2O + SO_2 = Hg_2Cl_2 + 2HCl + H_2SO_4$).

Impurity.—Corrosive sublimate, derived partly from the sublimation of any undecomposed mercuric chloride present, and partly from the decomposition of the calomel into mercury and mercuric chloride (dissociation). If a little of the calomel moistened with alcohol be heated on a clean knife-blade, a black spot will be formed on the blade should corrosive sublimate be present. The calomel may be purified from corrosive sublimate by thorough washing with water.

Properties.—(*a.*) *Physical.* A white, heavy, tasteless, insoluble compound. By the action of light some metallic mercury separates from it, rendering the calomel of a grey tint. Calomel may exist both in an amorphous and crystalline (four-sided prisms) condition. Sp. gr. 7·1. It sublimes before fusing. It is insoluble in alcohol, in cold dilute acids, and in water. By long-continued boiling in water, however, mercuric chloride will be formed, and mercury in fine subdivision precipitated.

The experimental vapor density of calomel (hydrogen being 1) is 119·2. If we allow Hg_2Cl_2 to be the molecule of calomel, occupying 2 vols. as a gas, its theoretical density is nearly double its experimental density (*i.e.*, $\frac{400(2Hg)+71(2Cl)}{2} = 235{\cdot}5$). If we regard the molecule as HgCl, then the actual and observed densities almost correspond. Why, then, do we not adopt HgCl as the formula for calomel ? For two reasons :—(1.) On the ground of the known atomicity of mercury ; and (2.) Because when mercurous salts are decomposed, they invariably form mercuric salts, free mercury being produced, thus favoring the notion that the molecule of the mercurous salt contains 2 atoms of mercury rather than one. *Can we then explain this anomalous vapor density of calomel ?* It is believed that at high temperatures the salt undergoes *dissociation* (*see* DISSOCIATION), the 2 volumes of mercurous chloride splitting up into 2 volumes of mercuric chloride and 2 volumes of mercury (making in all 4 volumes instead of 2 volumes), the mercury and mercuric chloride re-combining as the temperature is lowered. The vapor density of mercurous bromide is similarly anomalous.

(*β.*) *Chemical.* Lime water or a solution of sodic or of potassic hydrate decomposes mercurous chloride, the black mercurous oxide being formed ($Hg_2Cl_2 + CaO = Hg_2O + CaCl$). (This constitutes the mixture known as " black wash.") With aqueous ammonia, calomel forms the black compound Hg_2NH_2Cl ($Hg_2Cl_2 + 2H_3N = Hg_2NH_2Cl + NH_4Cl$), which is decomposed by gaseous HCl into Hg_2Cl_2 and NH_4Cl. When gaseous ammonia is allowed to act on mercurous chloride the compound $HgNH_3Cl$ is formed, which evolves ammonia when heated, leaving a residue of mercurous chloride. Sulphuric acid has no action upon mercurous chloride. Boiling nitric acid dissolves it, forming mercuric nitrate and mercuric chloride. Boiling hydrochloric acid, and solutions of sodic and ammonic chloride also dissolve it, precipitating the metal, and forming mercuric chloride.

(4.) Mercuric Chloride; *Chloride, Bichloride* or *Perchloride of Mercury; Corrosive Sublimate* ($HgCl_2$).

[*Molecular weight*, 271. *Relative weight*, 135·5. *Specific gravity of solid*, 5·42 ; *of vapor*, 9·8.]

Preparation.—(1.) By heating mercury in the presence of an excess of chlorine.

(2.) By subliming a mixture of mercuric sulphate and common salt. [A trace of MnO_2 is often added to oxidize any mercurous salt that might be present] ($HgSO_4+2NaCl=Na_2SO_4+HgCl_2$).

(3.) By dissolving either the metal in aqua regia or mercuric oxide in hydrochloric acid.

Properties.—(*a.*) *Physical.* A white, heavy, crystalline (octahedral) substance, having an acrid metallic taste. Sp. gr., 5·4. It sublimes at a low temperature, fuses at 509° F. (265° C.), and boils at 563° F. (295° C.), the vapors evolved being condensible and very poisonous. It is freely soluble in water (1 in 16 at 60° F., 1 in 3 at 212° F.), in alcohol (1 in 3 at 60° F., 1 in 1 at 212° F.), in ether (1 in 3), and in solutions of the alkaline chlorides. Ether dissolves it from its aqueous solution. It is intensely poisonous, and acts as a powerful antiseptic.

(*β.*) *Chemical.* A stable compound. The aqueous solution is acid to litmus, and is decomposed by light with the precipitation of calomel. It is soluble in HCl and in H_2SO_4 without decomposition. From its solution in the latter acid, it may be sublimed unchanged. Alkalies decompose it. It forms double salts with the alkaline chlorides, these being more soluble than mercuric chloride itself. Thus with ammonic chloride it forms the double salt called "*sal alembroth*" ($HgCl_2, 2NH_4Cl, H_2O$).

Corrosive sublimate is used in medicine, as an antiseptic, etc.

Mercuric Oxy-chlorides.—These are formed by combinations of mercuric chloride with mercuric oxide. Three of them (and indeed more) have been described, all being formed by the action of potassium carbonate on mercuric chloride, viz. :—

(1.) $2HgO,HgCl_2$. (2.) $3HgO,HgCl_2$. (3.) $4HgO,HgCl_2$.

No. 1 ($2HgO,HgCl_2$) is formed by adding a cold saturated solution of potassium hydric carbonate to eight or ten times its bulk of a cold saturated solution of mercuric chloride (red oxychloride).

No. 2 ($3HgO,HgCl_2$) is formed by mixing together equal volumes of the saturated solutions (yellow oxychloride).

No. 3 ($4HgO,HgCl_2$) is formed by adding a mercuric chloride solution to a large excess of a hydric potassium carbonate solution.

We may here remark that if a mercuric chloride solution be added to a solution of the *normal* sodic or potassic carbonate, a *yellow* mercuric oxide is precipitated; but that if it be added to a solution of the *hydric* sodic or *hydric* potassic carbonate (bicarbonate), a *red oxychloride* is formed.

(5.) **Mercur-ammonic Chloride.**—*Infusible white precipitate* (*mercurius precipitatus albus*) ($NH_2Hg''Cl$).

Preparation.—By adding an excess of a solution of ammonia to a solution of corrosive sublimate ($HgCl_2+2NH_3=NH_2Hg''Cl+NH_4Cl$).

Constitution.—The importance of this compound depends on the fact that it was the first recorded case where the mobility of hydrogen was recognised. White precipitate (that is the precipitate formed where *the ammonia is in excess*) may be regarded as ammonium chloride where the dyad Hg'' has replaced two atoms of monad hydrogen. Thus:—

NH_4Cl=*ammonic chloride*, and $NH_2Hg''Cl$=*white precipitate.*

If *the mercuric chloride be in excess*, the body $N_2H_4Hg_4Cl_6$ is formed. This may be regarded as a double molecule of ammonium chloride, in which four of the group $(HgCl)'$ has replaced four atoms of hydrogen. Thus:—

$N_2H_8Cl_2$ = 2 of *ammonium chloride*; $N_2H_4(HgCl)'_4Cl_2$ = the *precipitate.*

Properties.—When white precipitate is boiled with water a yellow powder is produced ($Hg_4N_2Cl_2,2H_2O$). Thus—

$$\begin{array}{ccccccc} 4NH_2Hg''Cl & + & 2H_2O & = & Hg_4N_2Cl_2,2H_2O & + & 2NH_4Cl. \\ \text{White precipitate} & + & \text{Water} & = & \text{Yellow precipitate} & + & \text{Ammonic chloride.} \end{array}$$

When white precipitate is boiled with potassic hydrate, it forms NH_3 and HgO. Thus—

$$\begin{array}{ccccccccc} NH_2Hg''Cl & + & KHO & = & NH_3 & + & HgO & + & KCl. \\ \text{White precipitate} & + & \text{Potassic hydrate} & = & \text{Ammonia} & + & \text{Mercuric oxide} & + & \text{Potassic chloride.} \end{array}$$

When white precipitate is heated to 608° F. (220° C.), a red crystalline powder is formed ($2HgCl_2,Hg_3N_2$). Thus—

$$\begin{array}{ccccccc} 6NH_2Hg''Cl & = & 3NH_3 & + & NH_3,HgCl_2 & + & 2HgCl_2,Hg_3N_2. \\ \text{White precipitate} & = & \text{Ammonia} & + & & + & \text{Red powder.} \end{array}$$

Mercuro-diammonic dichloride or *fusible white precipitate* ($HgCl_2$, $2NH_3$) is formed when a solution of ammonium chloride is boiled with white precipitate. Thus—

$$\begin{array}{ccccc} NH_2Hg''Cl & + & NH_4Cl & = & HgCl_2,2NH_3. \\ \text{White precipitate} & + & \text{Ammonic chloride} & = & \text{Fusible white precipitate.} \end{array}$$

White precipitate is used as a poison for destroying vermin.

Compounds of Mercury and Iodine.

6. Mercurous iodide ... ... Hg_2I_2.
7. Mercuric iodide ... ... HgI_2.

(6.) Mercurous Iodide (Hg_2I_2); *Green iodide of Mercury.*

Preparation.—(1.) By triturating 10 parts of mercury with 7 parts of iodine, using a little alcohol to moisten the mass.

(2.) By adding potassium iodide to a solution of mercurous nitrate.

Properties.—A yellowish-green powder, becoming dark colored when exposed to the light, subliming below the temperature required for its fusion, and fusing at 554° F. (290° C.). When sublimed, it assumes the form of yellow crystals, which when heated become of a deep red color, recovering their yellow tint on cooling. It is decomposed by heat into HgI_2 and Hg.

It is sparingly soluble in water, and insoluble in an aqueous solution of potassium iodide.

(7.) Mercuric Iodide.—*Biniodide* or *Red iodide of Mercury* (HgI_2). [*Molecular weight*, 454. *Relative weight*, 227. *Specific gravity of solid*, 62·5 ; *of vapor*, 15·708.]

It occurs native as *coccinite.*

Preparation.—(1.) By triturating 10 parts of iodine with 13 parts of mercury, and subliming the mixture.

(2.) By precipitating a solution of mercuric chloride with potassic iodide. [The HgI_2 is soluble in excess of both salts, the solution being colorless.]

Properties.—(*α*.) *Physical.* Mercuric iodide is dimorphous. If the crystals be octahedral, the color of the salt is red ; if they be rhomboidal, it is yellow. The yellow variety, however, is not stable at ordinary temperatures. Mercuric iodide is soluble in hot alcohol, but is insoluble in water. Heated to 302° F. (150° C.) the color of the compound changes from red to yellow, the yellow crystals after a longer or shorter time changing into the red variety with the evolution of heat. It fuses at 392° F. (200° C.), forming a yellow liquid, which volatilizes at a higher temperature. The vapor has a remarkably high specific gravity (15·708).

(*β*.) *Chemical.* It is soluble in the alkaline chlorides, in neutral ammonium salts, and in hydrochloric and hydriodic acids. With potassic or ammonic iodide it forms double salts. Thus potassic-mercuric iodide ($2(KI,HgI_2),3H_2O$) crystallizes out on cooling from a hot solution of mercuric iodide in potassic iodide. The iodide forms double salts with mercuric oxide, sulphide, and chloride, such as, *e.g.*, ($HgI_2,HgCl_2$) and ($HgI_2,2HgCl_2$).

The solution of mercuric iodide in a solution of potassic iodide containing potassic hydrate, constitutes the "Nessler test" for ammonia. This solution forms, with ammonia, a brown precipitate

(Hg''_2NI,H_2O), the reaction being expressed by the following equation:—

$$2HgI_2+3KHO+NH_3=Hg''_2NI,H_2O+3KI+2H_2O.$$

Compounds of Mercury and Sulphur.

8.	Mercurous sulphide	Hg_2S.
9.	Mercuric sulphide	HgS.

(8.) **Mercurous Sulphide.**—*Subsulphide of Mercury; Æthiop's mineral* (Hg_2S).

Preparation.—(1.) By passing sulphuretted hydrogen through a solution of mercurous nitrate.

(2.) By acting on mercurous nitrate or mercurous chloride with ammonium sulphide.

Properties.—A black substance, easily decomposed by heat ($Hg_2S = Hg+HgS$).

(9.) **Mercuric Sulphide.**—*Cinnabar* (=the native HgS); *Vermilion* (=finely-powdered HgS) (HgS).

[*Molecular weight*, 232. *Relative weight, anomalous*, 77·3, *i.e.*, 2 *volumes of mercury vapor* + 1 *volume of sulphur vapor form* (*not* 2 *volumes but*) 3 *volumes of mercuric sulphide vapor; that is, they unite without condensation. Molecular volume*, $\boxed{\quad}\boxed{\quad}\boxed{\quad}$. *Specific gravity of solid*, 8·2; *of vapor*, 5·5.]

Natural History.—It is found native both in crystals (hexahedra) and in masses. It constitutes the principal ore of mercury.

Preparation.—(1.) By adding a solution of mercuric chloride either to a solution of sulphuretted hydrogen, or to one of a soluble sulphide (black variety of HgS).

(2.) By triturating 6 parts of mercury with 1 part of sulphur (Black variety of HgS or Æthiop's mineral).

(3.) The red form of sulphide is prepared from the black, either by subliming the black variety in vessels from which air is excluded, or by the prolonged action upon the black sulphide of an alkaline sulphide containing an excess of sulphur.

(4.) By triturating 300 parts of mercury with 114 of sulphur, and digesting the product with a solution of potassic hydrate at 120° F. (48·9° C.) (Red variety of HgS).

Ordinary commercial preparation of vermilion.—100 parts of mercury are triturated with 38 parts of sulphur and a little water, and then digested with a solution of KHO (16 per cent.) at a temperature of 122° F. (50° C.), making up the water as it evaporates. So soon as the color is satisfactory, the product is thoroughly washed to remove any potash, which has a tendency to render the product of a brown color.

[N.B.—On passing H_2S through a solution of a mercuric salt, a *white* precipitate is first formed. This results from a small quantity of the mercuric sulphide first produced forming a double salt with the mercuric salt in solution.]

Properties.—(*a.*) *Physical.* There are two varieties of mercuric sulphide, viz., the black and the red. The black variety is converted into the red without chemical change. (*See* p. 547.)

The red compound, when heated, *air being excluded*, sublimes without fusing, the sublimate, in the first instance, being of a black color, becoming red on cooling. When heated *in the presence of air*, the sulphur of the sulphide burns off (as SO_2), and the metal is set free.

(β.) *Chemical.*—Mercuric sulphide is unaffected either by acids (except nitro-hydrochloric and hydriodic acids), or by alkalies unless ignited in contact with them, in which case the mercury sublimes, an alkaline sulphide and sulphate being formed—

$$4HgS + 8KHO = 4Hg + K_2SO_4 + 3K_2S + 4H_2O.$$

The sulphide forms compounds with metallic sulphides (*e.g.*, $K_2S,HgS,5H_2O$) and also with other mercuric salts. It yields a white compound with mercuric chloride. It is a very permanent body; hence its value as a paint.

COMPOUND OF MERCURY AND NITROGEN.

(10.) **Mercuric Nitride** (Hg''_3N_2) (*See* p. 310).

Preparation.—By heating mercuric oxide in a current of ammonia ($3HgO + 2NH_3 = Hg''_3N_2 + 3H_2O$).

Properties.—A dark, explosive powder. Ammonia and sublimed mercury may be obtained by heating the nitride cautiously with a caustic alkali.

OXY-SALTS OF MERCURY.

(11.) **Mercurous Sulphate** (Hg_2SO_4) is a white, crystalline powder, and is produced by adding dilute sulphuric acid to mercurous nitrate, or by *gently heating* a mixture of mercury and sulphuric acid. Slightly soluble in water.

(12.) **Mercuric Sulphate** ($HgSO_4$) is formed by heating together mercury and sulphuric acid *at high temperatures* ($Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O$).

Properties.—A white powder. Its color changes on heating. Decomposed at a red heat. It undergoes decomposition when acted on with water, an insoluble heavy, yellow, basic salt, the *trimercuric sulphate* (called also *basic sulphate*, or *turpeth* (*turbith*) *mineral*) being formed ($HgSO_4,2HgO$), together with a soluble acid sulphate.

(14.) **Mercurous Nitrate** (*Protonitrate of mercury*) ($(Hg_2)''2NO_3, 2H_2O$.

Preparation.—By digesting mercury in an excess of dilute nitric acid. If the mercury be in excess, a basic nitrate is formed, having the formula ($3(Hg_2)''2NO_3,Hg''_2O,H_2O$). This basic nitrate may be known from the normal salt by its becoming black when triturated in a mortar with sodium chloride, calomel being formed, and mercurous oxide separating. Thus—

$$\begin{array}{llcccccccc} (\alpha.) & (Hg_2)''2NO_3,2H_2O & + & 2NaCl & = & Hg_2Cl_2 & + & 2NaNO_3 & + & 2H_2O. \\ & \text{Normal mercurous} & + & \text{Sodic} & = & \text{Calomel} & + & \text{Sodic} & + & \text{Water.} \\ & \text{nitrate} & & \text{chloride} & & & & \text{nitrate} & & \end{array}$$

$$\begin{array}{llcccccccccc} (\beta.) & 3(Hg_2)''2NO_3,Hg''_2O,H_2O & + & 6NaCl & = & 3Hg_2Cl_2 & + & 6NaNO_3 & + & Hg_2O & + & H_2O. \\ & \text{Basic mercurous} & + & \text{Sodic} & = & \text{Calomel} & + & \text{Sodic} & + & \text{Mercurous} & + & \text{Water.} \\ & \text{nitrate} & & \text{chloride} & & & & \text{nitrate} & & \text{oxide} & & \end{array}$$

By the action of aqueous ammonia upon a solution of the salt, a black mercurous ammonic nitrate (Hg'_2NH_2,NO_3, *or* Hahnemann's soluble mercury) is precipitated.

(15.) Mercuric Nitrate ($2Hg''2NO_3,H_2O$).

Preparation.—By dissolving mercuric oxide (or metallic mercury) in an excess of nitric acid.

Several yellow basic nitrates, of which the compound ($Hg2NO_3$, $HgO,2H_2O$) is one of the most important, are precipitated by the action of water upon mercuric nitrate. From these compounds, by the continuous action of hot water, the nitric acid may be completely removed, until mercuric oxide only remains.

(16.) Mercuric Phosphate ($Hg_3P_2O_8$) is a white powder, formed when sodium phosphate is added to a solution of mercuric nitrate.

REACTIONS OF MERCURY COMPOUNDS.

Flame.—None.

Spectrum.—Bright lines in green and blue.

(A.) MERCUROUS COMPOUNDS :—

Caustic alkalies with soluble or insoluble mercurous compounds.—Black ppt. (Hg_2O).

Sulphuretted hydrogen and *ammonic sulphide.*—Black ppt. (Hg_2S), insoluble in HNO_3. Soluble in aqua regia.

Hydrochloric acid with soluble mercurous compounds.—White ppt. ($HgCl_2$); turned black by ammonia.

Potassic iodide.—Green ppt. (Hg_2I_2).

Stannous chloride.—White ppt. (Hg_2Cl_2), becoming grey on the addition of an excess of the precipitant (metallic mercury).

(B.) MERCURIC COMPOUNDS :—

Caustic alkalies.—Yellow ppt. (HgO).

Ammonia.—White ppt. of a mercur-ammonium compound.

Sulphuretted hydrogen.—White or orange ppt., becoming black (HgS). Ppt. insoluble in ammonium sulphide, or in HNO_3, or in HCl.

Potassic iodide.—Red ppt. (HgI_2), soluble in excess of both solutions.

Stannous chloride.—White ppt. (Hg_2Cl_2) as above, becoming black or grey in the presence of an excess of the precipitant, metallic mercury being formed.

If a piece of copper be immersed in a warm solution of a salt of mercury, metallic mercury will be deposited on the copper. Similarly, mercury is deposited on gold immersed in a solution of a mercury salt, if the gold be touched through the solution with a piece of clean iron. These deposits may be volatilized and condensed on cold surfaces, or changed into an iodide of mercury, etc.

All mercury compounds yield a sublimate of the metal when heated in a test tube with dry sodium carbonate.

THALLIUM (Tl).

Atomic weight, 204. *Molecular weight (probable),* 408. *Specific gravity,* 11·8 *to* 11·91. *Fusing point,* 561° F. (294° C.). *Specific heat,* 0·0325. *Atomicity, monad in thallous compounds* (′) ($TlCl$; OTl_2), *and triad in thallic compounds* (′′′) ($Tl'''Cl_3$).

History.—Discovered by Crookes in 1861, by means of its peculiar spectrum. This spectrum was first noticed in a deposit taken from the flue of a sulphuric acid manufactory in the Harz, where thalliferous pyrites had been used in the manufacture of the acid. (The word Thallium is derived from θαλλός, "green," the metal being so named from its peculiar spectrum.)

Natural History.—It occurs sparingly, but is nevertheless widely distributed in Spanish and Belgian pyrites. It is also found in a Swedish mineral called *Crookesite,* in certain mineral waters, and in some specimens of mica and lepidolite.

Extraction.—By treating the deposit contained in the flues of sulphuric acid chambers with water, and precipitating the thallous chloride from the clear solution with hydrochloric acid. By the action of sulphuric acid, the thallous chloride is re-converted into thallous sulphate, from the solution of which metallic thallium may be precipitated by the action of metallic zinc or of the galvanic battery. The metal thus obtained is then fused in a covered crucible under potassic cyanide.

Properties.—(*a.*) *Physical.* A heavy crystalline body, exhibiting, when freshly cut, a brilliantly metallic surface. It is softer than lead, leaving a bluish line when rubbed on paper. This line may be known from a lead line, by its turning yellow (oxidizing) after a short time. The metal crackles like tin when bent. It is diamagnetic. Its specific gravity varies from 11·8 to 11·91. Its specific heat is 0·0325. It is volatile at a red heat, and boils below a white heat. Its spectrum consists of one intensely green line.

(*β.*) *Chemical.* Thallium rapidly tarnishes in air at common temperatures. It does not decompose water below a red heat. When melted it rapidly oxidises, but it may be distilled in a current of hydrogen. It burns in oxygen, emitting a green light, and producing thallic oxide (Tl_2O_3). It combines energetically with the haloids, and also with sulphur and phosphorus. Dilute acids generally dissolve it. The action of both nitric and sulphuric acid upon it is energetic, whilst that of hydrochloric acid is slight.

In chemical position, thallium is more closely allied to the monatomic metal silver than to the alkaline metals in the sparing solubility of its chloride and the insolubility of its sulphide, whilst silver oxide, like thallous oxide, is slightly soluble in water, its solution exhibiting an alkaline reaction.

Compounds of Thallium (Tl = 204).

	COMPOUNDS.		Formulæ (General).
1	Thallous oxide		Tl_2O
2	„ hydrate		$TlHO$
3	Thallic oxide		Tl_2O_3
4	„ hydrate		Tl_2O_3,H_2O
5	Thallous chloride		$TlCl$
6	Thallic chloride		$TlCl_3$
7	Bromides, analogous to chlorides		$TlBr$ and $TlBr_3$
8	Iodides ditto		TlI and TlI_3
9	Thallous sulphide		Tl_2S
10	Thallic „		Tl_2S_3
11	Thallous carbonate		Tl_2CO_3
12	„ nitrate		$TlNO_3$
13	Thallic „		$Tl3NO_38H_2O$
14	Thallous sulphate		Tl_2SO_4
15	Thallic „		$Tl'''_2(SO_4)_37H_2O$
16	Thallous phosphates	Orthophosphates	H_2TlPO_4 HTl_2PO_4 Tl_3PO_4
		Pyrophosphates	$H_2Tl_2P_2O_7$ $Tl_4P_2O_7$
		Metaphosphate	$TlPO_3$

The Oxides of Thallium.—Both *Thallous Oxide* (Tl_2O) and *Thallic Oxide* (Tl_2O_3), are basic oxides, and form soluble crystalline salts.

(1.) **Thallous Oxide** (Tl_2O) is formed whenever a freshly-cut surface of the metal is exposed to the air. On placing the tarnished metal in water, this layer of the oxide is instantly dissolved. The solution of thallous oxide in water is alkaline, forming thallous hydrate ($TlHO$). Thallous oxide rapidly absorbs carbonic acid from the air. When electrolysed, it yields metallic thallium.

(2.) **Thallous Hydrate** ($TlHO$) is formed by the joint action of air and water on the metal, or by adding barium hydrate to a thallous sulphate solution and evaporating the filtrate. Soluble in water, the solution being very alkaline. Heated to 212° F. (100° C.) it becomes Tl_2O.

(3 and 4.) **Thallic Oxide** (Tl_2O_3) is formed when thallium is burnt in oxygen. A dark red powder, insoluble in water. It may be

prepared as a hydrate (Tl_2O_3,H_2O) by adding potassic hydrate to a solution of a thallic salt. It gives off oxygen at a red heat, becoming Tl_2O. It is soluble in hot sulphuric acid with the evolution of oxygen.

(5.) **Thallous Chloride** ($TlCl$) is formed (α) when the metal is burnt in chlorine, or (β) as a white curdy precipitate on adding a soluble chloride to a solution of a thallous salt or of thallous hydrate. By exposure to light it becomes of a violet tint. It readily fuses, and at a high temperature volatilizes. It dissolves (like $PbCl_2$) in boiling water (1 to 50), crystallizing out on cooling. It is less soluble if some hydrochloric acid be added to the water. With platinic chloride it forms the double salt $2TlCl,PtCl_4$, and with ferric chloride the compound $6TlCl,Fe_2Cl_6$.

When thallous chloride is warmed with a solution of sodium hypochlorite, a thallic oxyhydrate is formed ($TlHO_2$).

(6.) **Thallic Chloride** ($TlCl_3$).

Preparation.—By passing chlorine through water in which thallous chloride is suspended. A thallic oxy-hydrate ($TlHO_2$) is formed by the action of a caustic alkali upon it.

Intermediate chlorides are known, viz., Tl_4Cl_6 and Tl_2Cl_4.

Thallic bromide and iodide have been prepared.

(9.) **Thallous Sulphide** (Tl_2S) is formed either by adding hydric ammonium sulphide to a solution of a thallous salt, or by the action of sulphuretted hydrogen on a solution of the oxalate or acetate of thallium. Insoluble in water, in the alkalies or in their sulphides. Soluble in sulphuric and in nitric acids. Undergoes oxidation on exposure to air.

(10.) **Thallic Sulphide** (Tl_2S_3) is prepared by fusing thallium with an excess of sulphur.

(11.) **Thallous Carbonate** ($TlCO_3$), is prepared either by saturating a solution of the hydrate with CO_2, or by exposing the metal or a solution of thallous hydrate to the air.

(12.) **Thallous Nitrate** ($TlNO_3$) is prepared by the action of nitric acid on the metal.

(13.) **Thallic Nitrate** ($Tl3NO_38H_2O$) and (15.) **Thallic Sulphate** ($Tl_23SO_47H_2O$), are prepared by the action of nitric and sulphuric acids respectively on thallic oxide.

(14.) **Thallous Sulphate** (Tl_2SO_4), a body isomorphous with potassium sulphate, combines with aluminium sulphate to form an octahedral thallium alum ($Al_2'''Tl_2(SO_4)_4,24H_2O$).

REACTIONS OF THE THALLIUM COMPOUNDS.

1. They all impart a green color to flame, and produce the spectrum peculiar to the metal (*vide supra*), one bright green line being prominent.

2. The metal is reduced whenever a thallous salt is ignited with a mixture of charcoal and sodium carbonate.

3. The metal is precipitated when a piece of zinc is placed in a solution of a thallium salt.

(A.) THALLOUS SALTS.—1. *Soluble chlorides* or *bromides;* a white ppt. of thallous chloride ($TlCl$), or of thallous bromide ($TlBr$). (*See* Thallic Salts.)

2. *Soluble iodides;* a yellow ppt. of thallous iodide (TlI).

3. *Potassium chromate;* a yellow ppt. of thallous chromate.

4. *Platinic chloride;* a yellow ppt. of $2TlCl,PtCl_4$.

5. *Alkaline hydrates* and *carbonates;* no ppt. (*see* Reaction with thallic salts).

6. *Ammonium sulphide;* a brownish-black ppt. (Tl_2S), insoluble in excess.

(B.) THALLIC SALTS.—1. *Soluble chlorides* or *bromides;* no ppt. (*See* Thallous Salts.)

2. *Alkaline hydrates and carbonates;* a brown gelatinous ppt. ($TlHO_2$). (*See* Thallous Salts.)

3. *Oxalic acid;* a white ppt.

TUNGSTEN (W (Wolfram or Wolfranium) = 184).

Atomic weight, 184. *Specific gravity,* 19·13. *Specific heat,* 0·0334. *Atomicity tetrad* (^{iv}), *in tungstous compounds* (WO_2), *and hexad* (^{vi}), *in tungstic compounds* (WO_3).

History.—Obtained by Scheele, 1781.

Natural History.—It occurs as Scheelite ($CaWO_4$) as Wolfram ($MnWO_4,3FeWO_4$), and as a tungstate of lead ($PbWO_4$) and of copper. It is also found as Wolfram ochre (WO_3)

Preparation.—By reducing tungstic anhydride (WO_3) with charcoal at a white heat, or by submitting the chlorides to the action either of sodium or of a current of hydrogen.

Properties.—A white, hard, brittle, almost infusible metal. Its alloy with steel (5 per cent.) is intensely hard, and permanently magnetic in a high degree. In mass, the metal is not acted upon by air at ordinary temperatures, but when finely powdered, it burns in air, forming WO_3. Tungstic acid is formed either by the action upon the metal of nitric acid or of aqua regia, or by heating the metal with nitre, or by boiling it in an alkaline solution. It combines with chlorine when heated with it.

TUNGSTEN COMPOUNDS.

Tungstous oxide	WO_2.
Tungstic oxide or anhydride ...	WO_3.
Tungstic acid	H_2WO_4.

Hypotungstous chloride, bromide and iodide	WCl_2; WBr_2; WI_2.
Tungstous chloride	WCl_4.
Tungstic pentachloride	WCl_5.
Tungstic hexachloride	WCl_6.
Tungsten oxychlorides, etc. ...	$WOCl_4$. WO_2Cl_2. WO_2Br_2.
Tungstous sulphide	WS_2.
Tungstic sulphide	WS_3.

Tungstous Oxide (WO_2).—This is prepared by heating WO_3 in a stream of hydrogen, avoiding too high a temperature, otherwise complete reduction might be effected. It is a brown powder, and burns in air, firing spontaneously if freshly prepared (pyrophoric), WO_3 being formed. It is an indifferent oxide, not forming salts.

Tungstic Oxide.—*Tungstic anhydride* (WO_3).

Preparation.—By the ignition of ammonium tungstate (prepared by the action of ammonia on the residue left after treating calcic tungstate (Scheelite) with aqua regia).

Properties.—A yellow powder, insoluble in water and in most acids, but soluble in alkalies. Fusible at a high temperature. Becomes green on exposure to light.

When a *hot* alkaline solution is neutralized with an acid, a *yellow* precipitate of tungstic acid (H_2WO_4) is thrown down, but when a *cold dilute* solution is similarly treated, a *white* precipitate of H_2WO_4, H_2O ($= H_4WO_5$) is formed.

Tungstic Acid exists in several modifications :—

(α.) *Common tungstic acid* (H_2WO_4), has a yellow color and is insoluble in water. It is prepared by drying the compound (H_2WO_4,H_2O) over sulphuric acid. The normal tungstates are salts of this dibasic acid.

(β.) *Metatungstic acid* ($H_2W_4O_{13},7H_2O$), is a white body, soluble in water, and may be obtained by decomposing the barium salt with sulphuric acid.

(γ.) A colloidal tungstic acid, similar to colloidal molybdic acid, has been prepared.

Tungstates and Metatungstates.

The tungstates yield a precipitate with an acid in the cold. The metatungstates yield no such precipitate.

The **Tungstates** are a very complex class, numerous polytungstates having been described.

The normal sodium and potassium tungstates ($Na_2WO_4,2H_2O$), are prepared by adding tungstic anhydride to a fused alkaline carbonate.

The sodium salt (a paratungstate), which is used as a mordant and also for rendering muslin uninflammable, is prepared by roasting wolfram with soda ash, and extracting the residue so formed with water.

Tungsto-tungstates.—The tungstates combine with tungstous oxide (WO_2), to form compounds to which the name *tungsto-tungstates* has been given.

The **Metatungstates** are formed by heating the normal salt with tungstic anhydride. The sodium salt has the formula, $Na_2W_4O_{13}$, $10H_2O$.

Certain **Phospho-tungstates** (corresponding to phospho-molybdates), have been prepared.

Silico-Tungstic Acid ($H_8SiW_{12}O_{42}$). The compound of silica with tungstic acid is obtained by boiling an acid salt of an alkaline tungstate (a polytungstate) with gelatinous silicic acid. It may be obtained in a free state by first adding mercurous nitrate to a solution of one of its salts, and afterwards decomposing the mercurous silico-tungstate formed with hydrochloric acid. It forms both normal and acid salts.

Chlorides of Tungsten.—*Hypotungstous chloride* (WCl_2) is a grey powder, formed by heating WCl_4 in a current of CO_2. *Tungstic chloride* and *pentachloride* (WCl_5) are formed by heating WCl_6 in a current of chlorine, the distillate being collected in a cold receiver.

Tungstic hexachloride (WCl_6). *Preparation.*—By heating dry tungsten in a current of dry chlorine. (If air or moisture be present, an oxychloride ($WOCl_4$) would be formed.)

Properties.—A black crystalline mass, not altered by exposure to air unless $WOCl_4$ be present. Fuses at 527° F. (275° C.), and boils at 654·8° F. (346° C.). Undergoes dissociation above the boiling point. Soluble in bisulphide of carbon. Decomposed by boiling water into tungstic and hydrochloric acids.

Reactions of the Tungstates.

Solutions of the tungstates may be prepared by fusing the insoluble tungsten compounds with an alkali.

1. *Sulphuretted hydrogen* and *ammonic sulphide.* No ppt. (A brown precipitate of WS_3 is thrown down if HCl be added to the solution after the addition of ammonium sulphide.)

2. A *borax bead* heated in the reducing flame with compounds of tungsten gives a blue color, whilst in the oxidizing flame a yellow bead, changing to red on cooling, is formed.

3. If to solutions acidulated with HCl a piece of zinc be added (*nascent hydrogen*), a deep blue-colored liquid results.

SECTION III.—ORGANIC CHEMISTRY.

CHAPTER XIX.

Organic Compounds and Organised Bodies — Definition of Organic Chemistry—ORGANIC ANALYSIS — Ultimate Analysis—Vapor Density — Method of determining Vapor Densities—Proximate Analysis.

DISTINCTION BETWEEN AN ORGANIC COMPOUND AND AN ORGANISED BODY.

BY *an organic compound,* such, *e.g.*, as sugar, urea, etc., we mean a body of definite chemical constitution, exhibiting frequently, if solid, a crystalline structure, and possessing, if liquid, a fixed boiling-point. Many organic compounds have been formed artificially.

By *an organised body,* such, *e.g.*, as tissue, we imply a solid non-crystalline substance, of a fibrous or cellular nature (*i.e.*, non-crystalline), suffering decomposition when heated, so that it can neither be liquefied nor vaporised intact. No organised bodies have been formed artificially.

DEFINITIONS OF ORGANIC CHEMISTRY.

(1.) Organic chemistry was originally defined as "*the chemistry of compounds produced under the influence of a vital force,*" that is, of a force present only in the bodies of *living* plants and animals. Those who held this doctrine of a vital force, divided organic bodies into two classes :—

(*a*.) *Direct organic bodies ;* that is, bodies like sugar, starch, etc., actually formed in the living plant or animal ; and

(β.) *Indirect organic bodies ;* that is, bodies formed from direct organic bodies, by chemical or physical means. Thus oxalates and formates were regarded as belonging to organic chemistry, because the formates were prepared from the oxalates, and the oxalates from starch. Similarly, olefiant gas and alcohol were considered organic, because olefiant gas was produced from alcohol, and alcohol was formed from sugar. Starch and sugar being *direct* organic bodies the products derived from them were regarded as *indirect* organic bodies.

Recent researches, however, have shown that many organic compounds may be prepared artificially; we mean by that, without the medium of any organic substance. Thus, in 1828, Wöhler obtained urea from ammonium cyanate, this being the first instance of an organic compound being obtained by an artificial method. Here life, "the vital force," played no part. A solution of the cyanate was made and allowed to evaporate, when urea was deposited. *Cyanogen* may be obtained from sodium cyanide ($NaCN$), a salt prepared by passing nitrogen over a heated mixture of carbon and sodium carbonate. Alcohol (as Bertholet discovered in 1856) may also be built up artificially from its elements; and so on. Hence "the vital force" scarcely serves to mark the division between organic and inorganic chemistry.

(2.) Organic chemistry was defined by Laurent as "*the chemistry of carbon and its compounds.*" All organic substances contain carbon combined sometimes with hydrogen only, as in benzene (C_6H_6), and sometimes with nitrogen only, as in cyanogen (CN). Sometimes the carbon is combined with hydrogen and oxygen, as in sugar, alcohol, etc., and not unfrequently with nitrogen in addition, as, for example, in the vegetable alkaloids. Heating a substance in a test-tube, to see whether it chars, is the usual rough test for an organic body, and unless the body be volatile without decomposing, the result is accurate.

To accept this definition, however, in its integrity, would involve our placing carbonic oxide (CO) and carbonic anhydride (CO_2) with the carbonates amongst organic compounds. To meet this difficulty, Frankland defines an organic body as "a substance where one or more atoms of the carbon of a molecule are *directly* combined with carbon, nitrogen, or hydrogen." Thus he excludes carbonic anhydride, as a body in which the carbon is combined directly only with oxygen ($O{=}C{=}O$). Cyanic acid is an organic compound, because the carbon is directly combined with nitrogen ($N \equiv C{-}O{-}H$). The objection to this hypothesis is that it takes for granted our power of examining the internal molecular structure of bodies, whereas at present such insight is nothing more than mere speculation.

(3.) Organic chemistry was defined by Liebig as "*the chemistry of compound radicals.*" But compound radicals, as we have already seen, are not unknown in mineral chemistry. Silver nitrate, $Ag(NO_3)$, which consists of silver and the compound radical (NO_3), bears a close resemblance to silver acetate, $Ag(C_2H_3O_2)$, consisting of silver and the compound radical ($C_2H_3O_2$). Both salts part with their compound radicals when a soluble chloride is presented to them to form $AgCl$. Again succinic acid

$$\left.\begin{matrix} H_2 \\ C_4H_4O_2 \end{matrix}\right\} O_2 (= C_4H_6O_4)$$

bears a close resemblance to sulphuric acid

$$\left.\begin{matrix} H_2 \\ SO_2 \end{matrix}\right\} O_2 (= H_2SO_4)$$

each body containing a compound radical.

But although the existence of compound radicals can scarcely be regarded as peculiar to organic chemistry, nevertheless their presence is one very striking characteristic of it.

By a compound *organic* radical we mean "a group of atoms containing one or more atoms of carbon, of which one or more bonds are unsatisfied." (Frankland.) As in inorganic chemistry we have elements of different atomicities, so in organic chemistry we have radicals of different atomicities. For example, we find *univalent radicals*, such as methyl (CH_3), forming methylic chloride $(CH_3)'Cl$; *divalent radicals*, as ethylene (C_2H_4), forming ethylene chloride $(C_2H_4)''Cl_2$; *trivalent radicals*, as glycerile (C_3H_5), the radical of glycerine ($C_3H_5(HO)_3$), etc. Basic radicals are sometimes found combined with acid radicals, the whole body being in such case made up of compound radicals; as *e.g.*, in methylic acetate, $(C_2H_3O_2)CH_3$.

No mono-, tri-, or quinqui-valent radical can exist as a separate group any more than a monad (as hydrogen), a triad, or a pentad element (as nitrogen) can exist as a separate atom.

Having seen that it is impossible to draw any exact line dividing organic from inorganic chemistry, we may here note one or two special characteristics of organic bodies :—

1. The principal elements entering into the composition of organic bodies are few, *viz.*, carbon, hydrogen, nitrogen, and oxygen; at the same time nearly, if not every element, found in the mineral kingdom, is also to be found in the organs of the plants or of the animals that serve to elaborate these compounds.

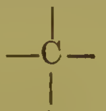
2. Although *the elements* of which organic bodies are formed are, as we have said, few, nevertheless the *number of atoms* constituting a molecule is frequently very large. No organic compound is known containing only two atoms in a molecule, and only one, *viz.*, hydrocyanic acid (HCN), containing three. In sugar 45 atoms, and in margarin 217 atoms, make up the molecule of these bodies respectively.

3. Organic bodies are remarkable for their complicated and elaborate constitution. This depends on two circumstances :—(α), the frequent occurrence of compound radicals in organic bodies; and (β) the chemical characteristics of the four elements of which organic compounds are chiefly composed.

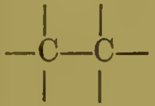
Respecting this latter point, *viz.*, the chemical values of the four elements of which organic bodies are chiefly composed, it is to be noted that carbon is a *tetrad;* nitrogen a *triad;* oxygen a *dyad*, and hydrogen a *monad.*

The tetravalent atomicity of carbon is important. It is regarded as "*fully saturated*" when it is combined either with 4 monads (as in CH_4), or with the equivalent of 4 monads, such as 2 dyads (as in CO_2) or 1 triad and 1 monad (as in CNH), etc. It is regarded as "*not saturated*" in compounds that contain less than 4 monads or their equivalent, such as CO. Under slight physical influences, however, such as light, the non-saturated compound CO will combine with Cl_2, forming *phosgene gas* ($COCl_2$), in which compound the carbon becomes fully saturated.

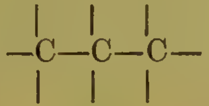
But a carbon atom will also combine with a carbon atom (Duplication). Two separate carbon atoms possess 8 unsatisfied bonds (four to each). When combined, however (forming a dicarbon atom), they have only 6 unsatisfied bonds, because it will be seen that one bond from one carbon atom combines with and satisfies one bond from the second carbon atom, thus satisfying 2 of the 8 bonds. Similarly, a combination of 3 carbon atoms (a tricarbon atom) has only 8 unsatisfied bonds instead of 12. Thus



$-\overset{|}{\underset{|}{C}}-$ = a carbon atom;



$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$ = a dicarbon atom;



$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$ = a tricarbon atom.

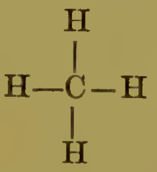
Thus the addition of every carbon atom increases the non-saturated bonds of a compound by 2. It will be seen, therefore, why we regard a series of bodies that increase by an addition of CH_2, as a homologous series; as, for example, in the monatomic methyl series:

thyl $(CH_3)'$	Methyl-hydride $(CH_3)H$	Methyl-chloride $(CH_3)Cl$	Methyl-alcohol $(CH_3)(HO)$
yl $(C_2H_5)'$	Ethyl-hydride $(C_2H_5)H$	Ethyl-chloride $(C_2H_5)Cl$	Ethyl-alcohol $(C_2H_5)(HO)$
pyl $(C_3H_7)'$	Propyl-hydride $(C_3H_7)H$	Propyl-chloride $(C_3H_7)Cl$	Propyl-alcohol $(C_2H_7)(HO)$
etc.	etc.	etc.	etc.

Types formed on carbon as the grouping agent in non-nitrogenized bodies, and on nitrogen in nitrogenized bodies. (Frankland.)

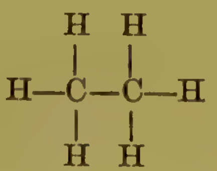
It may be conveniently noted here that Frankland regards these carbon groupings to which we have referred, as constituting a series of types of non-nitrogenous bodies. In the case of nitrogenized bodies, nitrogen is regarded as forming the grouping element. Thus—

(1.) The *single carbon atom type* has been termed the *monadelphic* or *marsh gas type.*



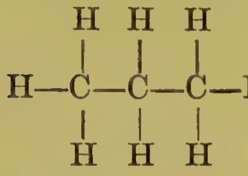
$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H = CH_4\text{, Marsh gas.}$$

(2.) The *dicarbon atom type* has been termed the *diadelphic* or *methyl type.*



$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H = \left\{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right. \text{Methyl.}$$

(3.) The *tricarbon atom type* has been termed the *triadelphic type.*



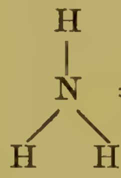
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

, as for example $\left\{\begin{array}{l}CH_3\\ CH_2\\ CH_3\end{array}\right. = C_3H_8$, Propyl-hydride,

and so on.

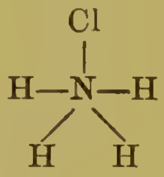
On the other hand nitrogenized bodies may be arranged under one of either of the following forms :—

(4.) The *ammonia type ;* represented thus—



$=N'''H_3$, Ammonia.

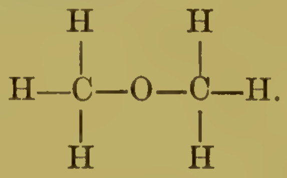
(5.) The *ammonic chloride type ;* represented thus—



$= N^{v}H_4Cl.$

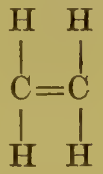
Frankland also describes—

(6.) The *double monadelphic type,*



$$H-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-H.$$

(7.) The *condensed diadelphic* or *olefine type,*



$$\underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}}$$

4. A great *variety of property* naturally occurs as the result of the complicated chemical constitution of organic bodies, some constituting our daily food, others being actively poisonous substances.

ORGANIC ANALYSIS.

The analysis of an organic body is of two kinds, viz., *proximate* and *ultimate.*

(1.) A *proximate analysis* of a body implies "the separation and estimation of its component or proximate principles"—

Thus : determining the presence and relative proportions of sugar, fat, casein, and salts in milk, constitutes "*a proximate analysis*" of milk.

(2.) An *ultimate analysis* of a body implies "the separation and the estimation of the constituent or ultimate elements"—

Thus: determining the presence and the relative proportions of carbon, hydrogen, nitrogen, and oxygen in the casein of the milk, constitutes "*an ultimate analysis*" of casein.

We commence our studies with the principles of, and the method of conducting, the ultimate analysis of organic bodies.

ULTIMATE ANALYSIS OF ORGANIC BODIES.

The principle of the ultimate analysis of a body containing carbon, hydrogen, and oxygen, may be stated as follows, viz.:—To burn a known weight of the organic body in oxygen, and to collect and weigh the oxidised products. The *carbon* is determined as CO_2, the *hydrogen* as H_2O, and the *oxygen* by difference—that is, by subtracting the combined weight of the hydrogen and carbon from the total weight of the material operated upon.

The conditions necessary for the success of the experiment are as follows:—(1.) That the body operated upon should be *pure;* (2.) that it should be *dry;* (3.) that it should be perfectly burnt; and (4.) that the products should be accurately weighed.

To insure the *purity* of a compound, a crystal (if the substance be crystalline) is to be preferred.

Fractional crystallization, or *fractional distillation*, or *fractional precipitation* are processes employed to separate two or more substances.

The question is all-important, and yet often full of difficulty, Is the substance under examination pure or not? If it be a liquid, we ask, Has it a fixed boiling point? If a gas, Has a diffused portion the same composition as the part not diffused? If a solid, Are the results of analysis, of its specific gravity and solubility at different temperatures, and of its fusing point, constant and uniform? (Pp. 2 and 3).

The history of ultimate analysis.—The first attempts at organic analysis were simply destructive distillation, the *products* of such distillation being regarded by the older chemists as *the elements* of organic bodies. Thus grew the dictum "air, oil, water and earth (caput mortuum) are the elements of organic bodies."

Hales and Priestly were the first who improved this process of destructive distillation by collecting the gaseous products evolved during the operation.

In 1810, Gay Lussac and Thénard suggested (in principle) the process of analysis which is now adopted, viz., burning the body in oxygen and collecting the products. Their process was as follows:—A glass tube, containing a weighed quantity of the organic body to be examined was placed in an upright position in a furnace. When the tube was sufficiently heated, oxygen was supplied to the organic matter by dropping potassium chlorate into the tube. The gases evolved were collected over mercury and *measured.*

The objections to this process were its practical difficulties, namely, (1,) the constant cracking of the tube, (2,) the frequent loss occasioned by the substance being blown out of the tube, (3,) the difficulty of ensuring the complete combustion of the organic matter, owing to the immediate and rapid generation of oxygen from the potassium chlorate, and (4,) the inaccuracies resulting from *measuring* the products of combustion.

Berzelius suggested the following improvements in the process, viz., (1,) placing the tube in a *horizontal* position; and (2,) modifying the violent action of the potassium chlorate by mixing it with common salt. Further (3,) he *weighed* the products, using for this purpose a chloride of calcium tube to collect the water, and fragments of caustic potash contained in a large glass bulb to collect the carbonic anhydride.

Gay Lussac and Thénard, Berard, Berzelius, and, lastly, Thompson, suggested the use of cupric oxide, instead of potassium chlorate, for the supply of the oxygen. Its advantages were—(1,) the comparative ease with which it could be obtained pure and dry; and (2), more particularly, that when heated alone it required a high temperature for its decomposition, but that when heated with organic matter, it readily imparted its oxygen to it.

Lavoissier, Saussure, and Prout suggested passing a stream of pure oxygen through the combustion tube instead of using cupric oxide.

Finally, Liebig improved the process in many of its details. He suggested the use of plumbic chromate as an oxidising agent, instead of cupric oxide, under the following circumstances:—

(*a.*) *When the compound contains chlorine or bromine.* When cupric oxide is used, the volatile bodies $CuCl_2$ and $CuBr_2$ are formed, which, condensing in the calcium chloride tube, introduce a source of error. This is avoided by the use of plumbic chromate.

(*β.*) *When the compound contains sulphur.* The sulphur, when burnt with cupric oxide, forms SO_2, which would be absorbed by the potassic hydrate solution, thus falsifying the results obtained by weighing the potash bulbs. With plumbic chromate, on the contrary, the sulphur does not form SO_2, but the non-volatile body plumbic sulphate.

(*γ.*) *When the compound contains alkaline salts.* The alkaline carbonates into which these alkaline salts are converted by heat, are not decomposed by contact with cupric oxide (thereby decreasing the quantity of free CO_2 formed), whilst they are decomposed by the action of plumbic chromate.

(δ.) When the compound is difficult of combustion.

(I.)—The Experimental Determination of the Carbon, Hydrogen, and Oxygen of an Organic Compound, not containing Nitrogen.

This is conducted as follows :—A tube of hard glass, eighteen inches long, drawn out to a narrow neck, and closed at one end, is filled for the first five inches with pure cupric oxide. An accurately-weighed quantity of the organic body to be examined, mixed with cupric oxide, is then introduced, the remainder of the tube being filled up with pure oxide. To this combustion-tube is attached—

First, an accurately-weighed tube containing *calcic chloride*, for the purpose of absorbing the moisture formed by the oxidation of the hydrogen, calcic chloride not absorbing carbonic anhydride ; and

Secondly, an accurately-weighed bulb-tube containing *a solution of potassic hydrate*, for the purpose of absorbing the carbonic anhydride formed by the oxidation of the carbon.

The front part of the combustion-tube (that is, the part containing pure cupric oxide) is first heated to redness. This done, the heat is next applied to the mixture of the oxide and the organic matter, ending at that part of the tube furthest from the absorption tube. Thus the organic body is burnt by the oxygen of the cupric oxide. The hydrogen of the organic body, as water, will be absorbed by the calcic chloride, and the carbon as carbonic anhydride will be absorbed by the potash solution.

Finally, the sealed end of the combustion-tube is broken off, and pure dry air or oxygen is drawn through the apparatus, so that any moisture or carbonic anhydride remaining in the tube when the operation is complete may be displaced and absorbed.

The tubes are then detached, and when cool, are again weighed. The increase in the weight of the chloride of calcium tube represents the water formed by the combustion of the hydrogen of the compound, and the increase in the weight of the bulbs containing the solution of potassic hydrate, represents the carbonic anhydride formed by the combustion of the carbon of the compound.

Determination of Oxygen.—The oxygen is calculated by difference ; that is, having proved the body to contain only hydrogen, carbon, and oxygen, the combined weights of the hydrogen and the carbon are subtracted from the total weight.

Method of Calculating Results.

Say 10 grains of sugar is burnt :—

(*a*.) The calcic chloride tube after experiment weighed 205·78 grs.
„ „ before „ „ 200·00 „

Therefore the product of the combustion of the hydrogen of 10 grains of sugar yields H_2O ... ... } = 5·78 grs.

It follows therefore—

H_2O H_2 Wt. of H_2O in 10 grs. of sugar.

$18 : 2 :: 5{\cdot}78 : x = 0{\cdot}643$ grs. of hydrogen in 10 grs. of sugar.

(β.) The potassic hydrate solution after expt. weighed 815·39 grs.
" " " before " 800·00 "

Therefore the product of the combustion of the carbon of 10 grains of sugar yields CO_2 ... ... } = 15·39 grs.

It follows therefore—

CO_2 C Wt. of CO_2 in 10 grs. of sugar.

$44 : 12 :: 15{\cdot}39 : x = 4{\cdot}198$ grs. of carbon in 10 grs. of sugar.

(γ.) 10 grs.—4·841 grs. (0·643 grs. of H + 4·189 grs. of C) = 5·159 grs. of oxygen.

(δ.) Multiplying these quantities by 10, we find that there are in every 100 parts of sugar—

Carbon	41·98 parts.
Hydrogen	6·43 "
Oxygen	51·59 "

Experimental Errors.—Usually our estimation of the carbon in a body is 0·1 to 0·2 per cent. *too low*, the error arising from the incomplete combustion of the body, whilst our estimation of the hydrogen is 0·1 to 0·2 per cent. *too high*, the error arising from the impossibility of effecting the entire removal of moisture.

In the case of a liquid it is commonly placed in the combustion-tube in a glass bulb, the exact weight of the liquid introduced being previously determined; whilst in the case of a fat or wax, etc., a little platinum boat is usually employed for the same purpose.

(II.)—Estimation of the Hydrogen and Carbon in a Body containing Nitrogen.

If the nitrogen were evolved as free nitrogen from the organic body its presence would not signify, inasmuch as pure nitrogen would neither be absorbed by the calcic chloride, nor by the solution of caustic potash. But as a rule, during a combustion analysis, a small quantity of the nitrogen of nitrogenised bodies becomes oxidized to nitric oxide (N_2O_2), which, on coming into contact with the air in the potash-bulb apparatus, would be further oxidized to nitric peroxide (N_2O_4), and would then be absorbed by the solution of potassic hydrate, and so interfere with the estimation of the CO_2.

To remedy this it is usual to place some copper turnings in the front part of the combustion-tube, and to maintain the metal at a red heat during the whole experiment. The action of the copper is as follows :—The red-hot copper decomposes any oxide of nitrogen formed, itself absorbing the oxygen, and setting free pure nitrogen, which merely escapes into the air, unabsorbed either by the chloride of calcium or by the solution of potassic hydrate.

(III.)—The Recognition and Estimation of the Nitrogen in an Organic Body.

The carbon and hydrogen of the substance having been first estimated by the process described above, the nitrogen must be determined by a separate experiment.

(1.) The Recognition of Nitrogen in Organic Bodies.—The presence of nitrogen may be known—

(*a.*) By heating the substance with a small piece of potassium (or sodium), dissolving the residue in water, adding to the clear filtrate a few drops of a mixed solution of ferrous sulphate and ferric chloride and an excess of hydrochloric acid. A blue precipitate (Prussian blue) indicates the presence of nitrogen.

(*β.*) By the setting free of ammonia when the organic body is heated with potassic hydrate.

(2.) Estimation of Nitrogen.—(A.) *By volume.* (*a.*) (Process of Dumas.) This process is applicable to the analysis of all nitrogenised substances.

The combustion-tube, sealed at one end, is prepared as follows :—The first five or six inches of the tube is filled with hydric sodic carbonate ($NaHCO_3$). The mixture of cupric oxide and the organic matter is next introduced, and afterwards some pure cupric oxide, the last two inches of the tube being filled up with copper turnings. A delivery-tube, the further end of which dips under mercury, is now fitted to the combustion-tube. The apparatus having been proved to be air-tight, a portion of the hydric sodic carbonate is heated. The carbonic anhydride generated sweeps the air out of the tubes. If this were not done the atmospheric nitrogen would vitiate the results. This done, a graduated tube, filled two-thirds with mercury and one-third with a solution of potassic hydrate (the latter to absorb the CO_2 generated during the experiment), is inverted over the delivery-tube. The copper in the combustion-tube is now made red hot, so that it may effect the decomposition of any oxides of nitrogen formed during the process. The pure cupric oxide is next heated, and then the mixture of the cupric oxide with the organic matter. The H_2O formed is condensed, whilst the CO_2 is absorbed by the potassic hydrate solution, the nitrogen alone collecting in the receiver. The combustion being complete, the undecomposed carbonate is heated, the carbonic anhydride generated sweeping any residual nitrogen from the combustion and delivery-tubes into the graduated receiver.

The volume of nitrogen formed is then read off, and corrections having been made for moisture, for temperature, and for barometric pressure, its weight is estimated from the corrected volume.

A slight experimental error, not exceeding 0·3 to 0·5 per cent., arises from a trace of nitrogen remaining in the tubes, and also being retained within the pores of the copper.

(β.) (Process of Frankland.) This process can be used when there is a very small quantity of the substance to work upon. The carbon and nitrogen are estimated in the same portion of the organic body by its combustion with cupric oxide, the gases produced being collected, measured and analysed.

A combustion-tube, about half an inch in diameter and 14 inches long, closed at one end, is charged as follows :—(1) About one inch is filled with granulated cupric oxide ; (2) a known weight of the organic substance, mixed with finer cupric oxide, is put in, and occupies about four inches of the tube ; (3) about three inches of granulated cupric oxide ; (4) a roll of reduced copper gauze ; and (5) one inch of cupric oxide. The open end of the tube is then drawn out before the blowpipe, and the narrow neck turned at right angles. The tube is then placed in a combustion furnace, and the open end attached to a Sprengel air-pump, the connection being made by means of a water joint.

The tube is then exhausted by means of the Sprengel, and the copper gauze heated to redness. After the removal of any gas that may have been occluded by the copper, the combustion is commenced by heating the tube gradually, beginning from the copper. When the whole tube is red-hot, the combustion is complete. The tube is again exhausted and the gas collected. This gas consists of carbonic anhydride, nitrogen, and nitric oxide. It is removed to the gas apparatus and analysed. From the volume of carbonic anhydride, nitrogen, and nitric oxide, the weight of carbon and nitrogen is determined.

(B.) *By weight.* (Process of Varrentrapp and Will.) We have noted that when nitrogenized organic matter is heated with sodic or potassic hydrates, the nitrogen is evolved as ammonia.* Advantage is taken of this reaction in estimating the nitrogen as follows :—

A known weight of the organic body is mixed with soda-lime. This is prepared by slaking lime (CaO) with a solution of sodic hydrate, and afterwards drying and igniting the product formed. The advantages of soda-lime over caustic soda are manifest. Caustic soda is very fusible, very deliquescent, very difficult to powder, and hence very difficult to mix with the organic body. Soda-lime, on the contrary, is infusible at a red heat, is not deliquescent, and, owing to the ease with which it can be reduced to a fine powder, admits of ready admixture with the organic body. The mixture of the organic matter with soda-lime is now placed in a glass combustion-tube, and heated. The ammonia evolved is conveyed into a tube containing hydrochloric acid, and the quantity of ammonia collected estimated as ammonic platinic chloride ($(NH_4)_2PtCl_6$), which may be either collected and weighed on a tared filter (100 grs. = 6·27 N), or else ignited in a crucible and the weight of the nitrogen estimated from the reduced platinum (100 grs. of Pt. = 14·18 N).

---

* When a non-nitrogenized organic body is heated with potassic hydrate, the carbon of the organic matter burns at the expense of the oxygen of the water of the hydrate, the carbonic anhydride formed combining with the alkali, and the hydrogen escaping.

The ammonia may also be estimated by collecting it in a measured quantity of dilute sulphuric acid of known strength, the amount of acid unneutralized being determined by titration (Peligot). This process of estimating the nitrogen as ammonia is not practicable, however, when the nitrogen is present as a nitro-compound, as *e.g.*, in nitro-benzol, ethyl nitrate, etc., or in the case of certain alkaloids, etc.

(IV.)—The Estimation of the Sulphur, Phosphorus and Haloid Elements in an Organic Body.

(1.) Estimation of Sulphur.—This is effected by one or other of the following processes :—(α.) By igniting a known weight of the organic substance with a mixture of nitre and potassic hydrate. An alkaline sulphate is thus formed, the sulphur of which may be estimated by precipitating its solution with baric nitrate (100 grs. $BaSO_4$ = 13·67 grs. of S).

(β.) By interposing between the calcic chloride tube and the potash bulbs in the combustion apparatus, a tube containing lead oxide, the sulphurous acid formed combining with the lead oxide to form a sulphate of lead ($PbO_2 + SO_2 = PbSO_4$).

(The presence of sulphur vitiates the accuracy of the carbon determination, when cupric oxide is used as the oxidizing agent. This does not occur when plumbic chromate is employed. *See* p. 562).

(2.) Estimation of Phosphorus.—This may be effected in a similar manner to the process (α.) already described for the determination of sulphur. After precipitating the sulphuric acid as $BaSO_4$, the excess of barium is to be thrown down with dilute sulphuric acid. The phosphoric acid present, the form in which the phosphorus now exists, is then to be estimated by supersaturating the solution with ammonia and adding magnesic sulphate. The ammonic magnesic phosphate precipitated is then collected, ignited, and weighed as $Mg_2P_2O_7$ (100 grs. = 27·92 grs. P).

(3.) Estimation of Chlorine, Bromine, and Iodine.—This is effected by heating the organic body in a tube with quicklime, whereby

$CaCl_2$, or $CaBr_2$, or CaI_2, is formed. The product is then dissolved in dilute nitric acid, and the chlorine, bromine, or iodine precipitated with argentic nitrate.

(4.) Estimation of Chlorine, Bromine, Iodine, Sulphur and Phosphorus in an Organic Body.—A mixture of three or four grains of the organic body with eighty grains of nitric acid (Sp. gr. 1·5), and a few crystals of argentic nitrate, contained in a sealed tube, is to be heated for three or four hours in an oil bath. When the tube is cold its contents are to be washed into a beaker. The insoluble AgCl, or AgBr, or AgI, which will be formed if the substance contains chlorine, bromine, or iodine, is then filtered off. The excess of silver present having been thrown down with hydrochloric acid, the sulphur and phosphorus in the clear filtrate are to be estimated as baric sulphate and ammonic magnesic phosphate respectively.

(5.) Other constituents remain as ash, and must be estimated in the usual manner.

VAPOR DENSITY.

Having determined by an ultimate analysis the exact chemical composition of a body, it is necessary (if the substance under examination be volatile) to determine the specific gravity of its vapor. We shall notice hereafter the important control that this determination exercises over the calculations derived from the ultimate analysis. We should here remark—

(*α.*) That with an organic, as with an inorganic compound, "its vapor density is one-half its molecular weight;" in other words, that the molecule of a compound body (no matter what number of atoms be present in the molecule) occupies in the state of gas twice the volume occupied by one atom of hydrogen ($H = 1$) under like conditions of temperature and pressure. Thus a molecule of water gas (H_2O) occupies two volumes, or □□, the atom of hydrogen (H) occupying one volume, or □.

(*β.*) It follows, if the molecule of a compound body in the state of vapor be twice the volume of an atom of hydrogen, that "*the specific gravity of any compound gas or vapor referred to hydrogen as unity, must be one-half its molecular weight.*" Thus—

The molecular weight of $H_2O = 18$. This, we have seen, occupies 2 volumes, *i.e.*, twice the volume occupied by H ;—

Therefore $\frac{18}{2} = 9$, the relative weight or vapor density of water gas, hydrogen being 1.

(*γ.*) But to this general law we find certain exceptions. These exceptions are probably more apparent than real, and may be explained by the circumstance that many bodies, when heated to their boiling point, decompose, so that the vapor experimented upon is not the pure vapor of the original body, but a mixture containing the vapors of the new compounds of decomposition. This form of decomposition is termed "*dissociation*" (*see* page 15). For example, a molecule of sulphuric acid (H_2SO_4), as a gas, is found to occupy not (as it should do) 2 volumes, but more than 2 volumes, the reason being that when sulphuric acid is heated above its boiling point, it is decomposed more or less completely into sulphuric anhydride and water ($H_2SO_4 = H_2O + SO_3$). Hence, if we were determining its vapor density, our experiment would be conducted, not with pure sulphuric acid vapor, but with a vapor containing the mixed decomposition products, viz.: water and sulphuric anhydride.

It will be evident that if *dissociation was complete*, the molecule of a substance (such, *e.g.*, as H_2SO_4) would occupy, in a state of vapor, 4 volumes instead of 2 volumes; that is, the H_2O formed would occupy 2 volumes, and the SO_3 2 volumes. This being the case, the observed specific gravity would be one-fourth (and not one-half) the molecular weight, the molecule appearing to occupy 4 times the volume of a hydrogen atom. But *dissociation may be, and usually is, only partial,* commencing at, or a little above, the boiling point, and becoming more and more complete as the temperature is increased.

The difficulty in determining vapor densities arising from dissociation, has been in some cases overcome by altering the relationship between the relative quantities of the products of dissociation, the tendency of compounds to combine being augmented by the presence of one of the compounds in excess. Thus, if we attempted to determine the vapor density of phosphoric chloride (PCl_5), we should find that it would split up into PCl_3 and Cl_2. If, however, we mix phosphorous chloride (PCl_3) with phosphoric chloride (PCl_5) the chlorine set free by heat from the PCl_5, being in the presence of a large excess of PCl_3 instantly combines with it to form PCl_5, enabling us at once to obtain the true vapor density of the phosphoric chloride. Thus in some cases the difficulties arising from dissociation have been met.

We now proceed to consider *the determination of vapor densities.*

Determination of Vapor Densities.

This may be effected in one of two ways; either

I. By determining the weight of a given volume of vapor: or

II. By determining the volume of a given weight of the substance.

I.—*By determining the weight of a given volume of vapor* (Process of Dumas).

(*a.*) Provide either a clean dry glass flask, or one of porcelain, if glass will not stand the necessary heat. The flask must have a long and finely drawn out neck, and be capable of holding from 200 to 300 c.c. Weigh the flask accurately, noting at the time the temperature and pressure.

Thus we learn the weight of the flask filled with air at a definite temperature and pressure.

(β.) Introduce now into the flask a quantity (say 50 to 100 grains) of the substance to be examined, and place the flask containing the compound in a water, oil, or mercury bath, the neck of the flask being external to the bath. The temperature of the bath employed must be considerably above the boiling-point of the body under examination. Hence the vapors of cadmium (860° C.), or of zinc (1040° C.), must be used if necessary. The vapor of the substance, as it is evolved, expels the air from the flask. When the evolution of vapor from the flask ceases, the neck of the flask is to be sealed, the temperature of the bath and the atmospheric pressure being noted at the time. When the flask is cold it is weighed, the temperature and pressure being again recorded.

Thus we learn the weight of the flask filled with the vapor of the substance under examination, at a definite temperature and pressure.

(γ.) The extreme point of the flask is now to be broken off under mercury. If the air of the flask has been entirely expelled, the mercury immediately rushes into, and completely fills the flask. By weighing the mercury that thus enters the flask, the capacity of the flask may be determined.

Thus we learn the capacity of the flask.

If, however, the mercury does not completely fill the flask, it proves that the expulsion of the air by the vapor was not complete. Under these circumstances, weigh *first* the mercury that enters the flask, and, *secondly*, the total mercury required to fill the flask.

Thus, by the difference between these two weighings, we learn the quantity of residual air in the flask at the time of the experiment, whilst the weight of the mercury required to fill the flask, gives us the gross capacity of the flask.

Example (from Roscoe).—A volatile hydro-carbon (C_6H_{14}) is taken for the experiment. The barometric pressure is throughout taken at 760 mm.

Weight of the flask filled with air (temperature 15·5° C.)	= 23·449 grms.
Weight of the flask filled with the vapor of the hydro-carbon (temperature 110° C.) ...	= 23·720 grms.
Capacity of the flask...	178 c.c.

From these data we enquire—

(1.) *What bulk would* 178 *c.c. of air at* 15·5° C. (the temperature at which the flask containing air was weighed) *occupy at* 0° C. (the standard temperature, *see* p. 40) ? Ans. 168·4 c.c.

(2.) *What is the weight of this volume of air?* Every c.c. of air at 0° C. and 760 mm. weighs 0·001293 grms. Therefore 0·001293 × 168·4 = 0·218 grms., the weight of 168·4 c.c. of air at 0° C., and 760 mm. pressure; in other words, the weight of the air the flask contains at 0° C.

(3.) The weight of the flask without air is therefore 23·231 grms. [23·449 grms. (flask + air)—0·218 grm. (weight of air) = 23·231 grms. (weight of flask).]

(4.) The weight of the flask filled with vapor is 23·720 grms. If we subtract from this the weight of the flask, we obtain the weight of the vapor in the flask [23·720 (flask + vapor) —23·231 (weight of flask) = 0·489 grm. (the weight of the vapor)].

(5.) 178 c.c. of hydrogen at 110° C. weighs 0·01134 grm. (1 c.c. of hydrogen at 0° C. and 760 mm. weighs 0·0008936 grm. (*see* page 43).

$$\text{Therefore } \frac{0·489}{0·01134} = 43·13 \left\{ \begin{array}{l} \text{The density of the vapor of } C_6H_{14} \\ \text{compared to hydrogen as unity.} \end{array} \right.$$

In this example we have omitted such minor details as the expansion of the glass flask, the errors of the thermometer, etc. If the pressure varied during the experiment, due allowance would have to be made.

If the air be not wholly expelled from the flask by the vapor, the residual air must be deducted from the total capacity of the flask, and the calculation made on the result.

II.—The vapor density may also be estimated "by determining the volume of a given weight of the substance."

(*a*.) (Process of Gay Lussac.)—A sealed glass bulb, containing a known weight of the substance to be examined, is introduced into a graduated tube full of, and standing over, mercury. The whole apparatus is then lowered into a bath of hot oil or other liquid, the heat of which bursts the glass bulb, and converts the whole of the volatile substance contained therein into vapor. The volume of vapor is then noted, and also the temperature of the bath, the atmospheric pressure, the height of the mercury in the graduated tube (the downward weight of which tends to *expand* the vapor), and the depth of the oil bath pressing on the mercury (the downward weight of which tends to *contract* the vapor). From these data, the vapor density may be calculated.

Hofmann's modification of the above process consists in enclosing the graduated glass tube in a second and larger tube, through which currents of the vapor of water or other body can be passed. In this way the trouble of lowering the whole apparatus into the oil bath is avoided. The volume of the vapor, the temperature, the pressure, and the height of the mercury column must be noted. The weight of hydrogen, which under the same conditions would occupy a similar volume, is then estimated, and

$$\frac{\text{the weight of substance examined}}{\text{the weight of hydrogen}} = \left\{ \begin{array}{l} \text{the vapor density} \\ \text{required.} \end{array} \right.$$

(β.) (Method of Victor and Carl Meyer.)—The apparatus consists of a glass vessel of about 100 cubic centimetres capacity, having fused to it a glass tube about 600 millimetres long, which can be closed at the top by means of an indiarubber stopper. To this glass tube, about 20 millimetres from the top, is fused a side delivery tube. The glass vessel is immersed in a bath containing a liquid, heated to a temperature above that of the boiling-point of the substance to be tested. The delivery tube dips into a trough containing water, so that over it a graduated gas tube can be placed.

When the vessel has reached a constant temperature (when the air ceases to bubble out of the delivery tube), the stopper is removed, and a known weight of the substance is quickly thrown in, the stopper replaced, and the graduated gas tube placed over the delivery tube. When the substance reaches the bottom it quickly evaporates, and displaces the air, which is collected and measured. All the data required are the weight of substance, the volume of air displaced, and the temperature and pressure at which the displaced air is measured. The exact temperature of the bath is not required, but the amount of substance taken must be such as, when in the state of vapor, will not occupy more than half the volume of the vessel. To calculate the vapor density

Let W = weight of substance taken.
V = volume of air measured.
B = barometric pressure.
t = temperature.
a = tension of aqueous vapor.

$$\text{Then vapor density} = \frac{W \times 760\,(1 + {\cdot}00366\,t).}{(B-a)\,V \times 0{\cdot}001293.}$$

We have now to consider—

The Application of the Facts deduced from the Ultimate Analysis, and from the Determination of the Vapor Densities of Organic Bodies.

(1.) *We learn firstly, the percentage composition of a body.* This, as we have noticed, is at once deduced from the analysis. Thus it was shown that every 100 parts of sugar contained—

Carbon, 41·98 ; hydrogen, 6·43 ; oxygen, 51·59.

(2.) From this percentage composition is deduced *the empirical formula* of the body, *i.e.,* the simplest possible expression of the relative quantities of the several elements present. Thus the empirical formula for sugar is $C_{12}H_{22}O_{11}$. The rule for estimating the empirical formula from the percentage composition is as follows :—" Divide the percentage numbers by their respective atomic weights, and divide these quotients by their greatest common divisor," thus—

	Percentage composition of sugar.		At. Wt. of element.		
Carbon............	41·98	+	12	=	350.
Hydrogen.........	6·43	÷	1	=	643.
Oxygen	51·59	÷	16	=	323.

The relationship between $C_{350}H_{643}O_{323}$ (dividing each by 30) is *very nearly* expressed by the formula $C_{12}H_{22}O_{11}$.

Very nearly, we say, but *not exactly*, for it has been already remarked (page 564) that slight experimental errors are inseparable from an ultimate analysis. This experimental error may be checked, amongst other methods mentioned under the determination of the molecular formula, by *reckoning back* the formula deduced to the percentage composition, as well as calculating the percentage composition into the formula. The question is—Do the errors fall, both as regards (1) *direction* and (2) *amount*, within the recognised experimental errors, remembering that as regards (1) *direction*, the carbon is commonly deficient and the hydrogen in excess, and that as regards (2) *amount*, the deficiency of the one or the excess of the other, should not exceed 0·1 or at most 0·2 per cent. ?

Thus in the case of sugar—

I.

From the percentage composition:

Carbon	41·98
Hydrogen	6·43
Oxygen	51·59

we calculate the formula:—

$C_{12}H_{22}O_{11}$

II.

From the formula $C_{12}H_{22}O_{11}$, we calculate the percentage composition as follows:—

Carbon	42·11
Hydrogen	6·43
Oxygen	51·46

This close correspondence of results proves the accuracy of the formula $C_{12}H_{22}O_{11}$.

(3.) Our results, further, help us to determine the *molecular formula* of the body. By this we mean "*the atomic constitution of the molecule, which, converted into vapor, corresponds to the volume formed by* 2 *atoms of hydrogen* (hence called a 'two-volume formula') *under similar conditions of temperature and pressure.*" The advantage of the molecular over the empirical formula is, that it represents not only the number of parts by weight, but also a quantity which, as a gas, occupies a known volume (*viz.*, 2 volumes). Comparison is thus simplified :—

(*a.*) *What is the relationship between the empirical and the molecular formula of a body?*

(1.) They may be identical ;

(2.) If not identical, the molecular formula is always some simple multiple of the empirical formula. Thus—

CH represents the empirical formula for benzene ;
C_6H_6 „ molecular „ „

We next enquire—

(β.) *How is the molecular* (or *two-volume*) *formula determined?*

(1st.) By the actual determination, when possible, of the vapor density. The vapor density of a body (that is, the relative weight of one volume) is always one-half the molecular weight (that is, the weight of two volumes).

CH, we learn from its ultimate analysis, represents the simplest expression of the relative amounts of carbon and hydrogen in the liquid called benzene. For in every 100 parts of benzene there are found on analysis to be—

92·3 parts of carbon
7·7 „ hydrogen.

From these numbers we derive the formula as follows :—

$$C : \frac{92 \cdot 3}{12} = 7 \cdot 7$$

$$H : \frac{7 \cdot 7}{1} = 7 \cdot 7.$$

The ratio of C : H is as 7·7 : 7·7 or as 1 : 1. Therefore CH is the empirical formula. From this formula we should estimate the vapor density of benzene as 6·5 ; thus—

$$CH = \frac{12 + 1}{2} = 6 \cdot 5.$$

Experiment, however, shows that the vapor density of benzene is 39 or 6·5 × 6. Hence, C_6H_6 must be the molecular formula—

$$C_6H_6 = \frac{72 + 6}{2} = 39 \cdot 0.$$

Or we may state the facts thus:—The parts by weight of benzene represented by the formula CH, when converted into vapor, only measure one-sixth of the volume produced by 2 unit weights of hydrogen ; whilst the parts by weight represented by the formula C_6H_6, measure, when converted into vapor, the volume produced by 2 unit weights of hydrogen, under similar conditions of temperature and pressure. Hence C_6H_6 is regarded as the molecular formula for benzene.

(2ndly.) It is, however, not always possible to estimate the vapor density of a body, for it may be non-volatile, or it may decompose when heated. Hence other means must be adopted to determine the parts necessary to form two volumes, *if the substance could be volatilized unchanged.*

(*a*) Such methods consist in *the analysis of the compounds the substance forms with well-known bodies*, in other words, its powers of combination and saturation.

(1.) In the case of organic acids or salt radicals, the silver or lead salt is commonly examined. For example, suppose we were determining the molecular formula of acetic acid. From the ultimate analysis we learn that CH_2O constitutes its empirical formula. One atom of silver will replace (we know) one atom of the hydrogen of the acetic acid to form acetate of silver. By analysis we find that every 100 parts of this acetate of silver contain—

Silver	64·68 parts.
Carbon, hydrogen, and oxygen	35·32 ,,

Hence the atoms of C, H, and O, combined with 108 atoms of silver (108 being the atomic weight of silver), may be found by the equation—

$$64{\cdot}48 : 36{\cdot}32 :: 108 : x = 58{\cdot}98.$$

To this 58·98 add 1 (=59·98), to allow for the hydrogen displaced by the silver. Hence the molecular weight of glacial acetic acid is 59·98, and its molecular formula (allowing for experimental error) must be $C_2H_4O_2$. Thus—

$$\begin{aligned} C_2 &= 24, \\ H_4 &= 4, \\ O_2 &= 32 = 60{\cdot}00, \text{ or } 59{\cdot}98 \text{ nearly.} \end{aligned}$$

(2.) In the case of organic bases, the neutral compounds formed with well-known mineral or organic acids, must be examined.

(β.) The study of the substitution products the body forms.

(γ.) The action of reagents.

(δ.) The calculation of the specific heat, and of the specific gravity of the body.

It is most important to bear in mind exactly what a molecular formula teaches, and what it does not teach :—

(α.) *It teaches* the actual chemical composition of a body, and its vapor density.

(β.) *It does not teach* the chemical formation of a body, nor its mode of decomposition ; nor does it help us in the least degree to distinguish isomeric modifications.

To supply these wants, *Rational*, *Constitutional* or *Structural Formulæ* are employed. A rational formula is designed to teach something of the nature and properties, and also the formation and decomposition of a substance.

It will be, of course, understood that rational formulæ are *theoretical* formulæ, and merely represent probabilities. They are not to be regarded as *actual representations* of the constitution of a body, but merely as the best representations our present knowledge enables us to form.

One compound may possess many rational formulæ, and we use them according to the decomposition or reaction we desire to represent. Thus, acetic acid ($C_2H_4O_2$) has numerous rational formulæ, amongst which we may mention the two following as illustrations of a condensed chemical language :—

(1.) $H(C_2H_3O_2)$: This implies that acetic acid is a *monobasic acid*, the one H placed on one side implying that it differs from the other three in its capacity for being replaced by a monad metal or alcohol radical. Thus we have the bodies—

$Ag'.C_2H_3O_2$	...	...	Argentic acetate.
$Ba''.(C_2H_3O_2)_2$	...	...	Barium acetate.
$(C_2H_5)'.(C_2H_3O_2)$	...	...	Ethyl acetate.

(2.) $C_2H_3O(HO)$: When phosphorous pentachloride acts on acetic acid, one of chlorine takes the place of one of the group (HO) (α); and when the acetic chloride thus formed is acted on with water, one of the group (HO) takes the place of 1 of chlorine (β), as will be seen in the following equations. This formula denotes, therefore, the linking together of the H and O to form (HO).

$$(\alpha.)\ C_2H_3O.(HO)+PCl_5=C_2H_3O.Cl+HCl+POCl_3.$$
$$(\beta.)\ C_2H_3O.Cl+H_2O=C_2H_3O(HO)+HCl.$$

PROXIMATE ANALYSIS OF ORGANIC BODIES.

By a proximate analysis is implied the separation of the *proximate principles* of bodies, as, *e.g.*, the separation of milk into fat, sugar, casein, etc. We can lay down no general rules for a proximate, as we are able to do for an ultimate analysis, each substance requiring special treatment.

The *microscope* and microscopic reactions afford great aid in proximate analysis, enabling us to detect and to identify various bodies, such as, *e.g.*, *starch cells* by their appearance and reaction with iodine; *cellulin*, by its turning blue with iodine, after having been first moistened with dilute sulphuric acid; *woody tissue*, by its being darkened by sulphuric acid, and turning brown on being afterwards treated with iodine; *corky tissue*, by the absence of any change with sulphuric acid or with iodine, etc., etc. Further, in separating crystallizable bodies, the microscope enables us to detect admixtures by the presence of crystals of different orders.

Dialysis, again, as a means of separating crystalloids from colloids, affords invaluable aid.

The following are the chief physical and chemical means adopted for separating the proximate principles of organic bodies.

1. *By spontaneous exudation*, as, *e.g.*, gums, resins, etc.
2. *By mechanical pressure*, as, *e.g.*, oils (linseed, castor, etc.).
3. *By the action of heat.*—This may be employed either—

(α.) To melt out resins and fats, or

(β.) To sublime the volatile acids (benzoic), or

(γ.) To distil the volatile oils, or

(δ.) To separate admixtures of volatile liquids by fractional distillation.

4. *By the action of solvents*:—

(α.) *Water* { *cold* — to dissolve gums, sugar, certain coloring matters, etc.
boiling — to dissolve starch, salts, etc.

(β.) *Alcohol*—to dissolve volatile oils, resins, certain alkaloids, coloring matters, etc.

(γ.) *Ether*, *chloroform*, or *benzol*—to dissolve fixed oils, camphor, caoutchouc, certain alkaloids, etc.

(δ.) *Dilute acids and alkalies*—the use of which, however, is generally to be avoided, owing to the changes they induce in the organic body itself.

CHAPTER XX.

THE NATURAL AND ARTIFICIAL CHANGES OF ORGANIC BODIES.

Fermentation—Varieties—I. Alcoholic—II. Lactic—III. Butyric—IV. Mucous—V. Acetous—Conditions necessary for Fermentation—Circumstances influencing Fermentation—Theories to account for it—Practical Applications. Putrefaction—Disinfectants. Eremacausis. Action of Heat—Action of Acids—Action of Alkalies—Action of Haloid Elements—Action of Nascent Oxygen and Hydrogen—and of other Reagents—Action of Light and Electricity.

The transformations which organic bodies undergo are twofold:—(A.) *Natural or Spontaneous*; and (B.) *Artificial.*

A.—NATURAL AND SPONTANEOUS.

It may be stated generally, that all organic substances are naturally prone to resolve themselves into simpler parts or groups. This resolution is effected in one of three ways:—

I. By Fermentation.
II. By Putrefaction.
III. By Eremacausis or Decay.

I. FERMENTATION.

Definition.—"A process whereby certain organic substances, under the influence of contact with a nitrogenous body called a ferment, are resolved into simpler groups." We may note that fermentation is accompanied by the development of certain minute living organisms, the existence of which may be either a *cause* or a *consequence* of the chemical change; that no offensive odors are evolved during the process; and that the products are most often of a useful nature.

We shall investigate the subject of fermentation in the following order:—

1. Its principal varieties.
2. The conditions necessary for its existence.
3. The conditions influencing its action.
4. The theories to account for it.
5. Its practical applications.

(1.) The Varieties of Fermentation.

There are five varieties of fermentative action, their distinctive names being derived from the principal product furnished :—

(α.) *The alcoholic* or *vinous fermentation,* in which *alcohol* is formed.

(β.) *The lactic fermentation,* in which *lactic acid* is formed.

(γ.) *The butyric fermentation,* in which *butyric acid* is formed.

(δ.) *The mucous* or *viscous fermentation,* in which a gummy matter is ormed.

(ε.) *The acetous fermentation,* in which *acetic acid* is formed.

(α.) **The Alcoholic or Vinous Fermentation:** *i.e.,* a fermentation characterised by the formation of alcohol. This results from the action of yeast on a solution of grape sugar, ethylic alcohol and carbonic anhydride being the chief products. The change of 95 per cent. of the sugar thus fermented may be represented as follows :—

$$\underset{\text{Grape sugar}}{C_6H_{12}O_6} = \underset{\text{Ethylic alcohol}}{2C_2H_6O} + \underset{\text{Carbonic anhydride.}}{2CO_2}$$

But besides these, other products are formed from the remaining 5 per cent. of sugar ; *viz.,* free hydrogen, the homologues of ethylic alcohol (as propylic, butylic, etc.), a hydrocarbon of the C_nH_{2n+2} series, glycerine (to the extent of 3 per cent. of the sugar fermented (Pasteur)), mannite, acetic acid, succinic acid (0·5 per cent.), etc. Many of these products are, however, no doubt the result of secondary action, either of the nascent hydrogen (as, *e.g.,* in the production of glycerine, mannite, etc.), or of the nascent oxygen (as, *e.g.,* in the production of succinic acid) resulting from the decomposition of water, which decomposition, it is believed, always occurs during the process.

The active agent of alcoholic fermentation is believed to be the cells of the *torula cerevisiæ.*

It is to be specially noted that cane-sugar and its isomerides (*i.e.,* the $C_{12}H_{22}O_{11}$ group) will not undergo vinous fermentation, this action being limited to grape-sugar and its isomerides (*i.e.,* the $C_6H_{12}O_6$ group). The change, however, of cane-sugar into grape-sugar, under the influence of a ferment, is rapid, the specific gravity of the liquid increasing as the change takes place, a solution of cane-sugar having a lower gravity than one containing an equivalent amount of grape-sugar.

(β.) **The Lactic Acid Fermentation,** *i.e.,* a fermentation characterised by the formation of lactic acid. This results from the action of putrefying cheese or milk on grape or milk-sugar. It is necessary, in order to neutralize the lactic acid as soon as formed, that the solution should contain either chalk (in which case a calcium lactate is produced), or zinc white (when a zinc lactate results), the presence of a trace of free acid entirely preventing the continuance of the fermentation by coagulating the casein and rendering it insoluble. This change into lactic acid may be represented as follows :—

(α.) $C_6H_{12}O_6$ (glucose) $= 2C_3H_6O_3$ (lactic acid).

(β.) $C_{12}H_{22}O_{11}$ (lactose) $+ H_2O = 4C_3H_6O_3$ (lactic acid).

Mannite is also formed during the process. It is necessary that the lactates themselves should be removed from the action of the ferment as soon as possible, otherwise they are converted into butyrates. The lining membrane of the stomach of the calf (rennet) and animal membranes generally, are specially active in inducing this variety of fermentation. In the case of milk, the casein acts as the ferment on the milk-sugar. Hence milk contains both the ferment itself, and the body to ferment.

The active agent of the lactic acid fermentation is believed to be the *penicillium glaucum.*

(γ.) **The Butyric Fermentation,** *i.e.*, a fermentation characterised by the formation of butyric acid.

This results from *the prolonged action* of the lactic acid ferment on the lactic acid, whereby butyric acid (which by the action of chalk is converted into butyrate of lime) together with free hydrogen, carbonic anhydride, acetic and caproic acids, are formed. The butyric fermentation is in fact the advanced stage of the lactic acid fermentation. Thus :—

$$2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2.$$

Lactic acid = Butyric acid + Carbonic anhydride + Hydrogen.

The active agent of the butyric fermentation is believed to be the same as that of the lactic fermentation, viz., the *penicillium glaucum.*

(δ.) **The Mucous or Viscous Fermentation,** *i.e.*, a fermentation characterized by the formation of gummy matters. This results from the action of certain nitrogenous substances on sugar, a gum (arabin), mannite ($C_6H_{14}O_6$) a non-crystallizable sugar, and lactic acid, forming the products. This fermentation commonly results in fermenting the juice of the sugar beet. It sometimes occurs in sweet *white* wines that have been kept too long, the action being capable of arrest by the addition of a little alum or sulphurous acid to the wine. It does not occur in *red* wines, the astringent matter derived from the grape skins preventing them from becoming "ropy."

(ε.) **The Acetous Fermentation,** *i.e.*, a fermentation characterized by the formation of acetic acid.

This results from the action of the acetous ferment (the *mycoderma aceti*) on alcohol. The action does not take place with pure alcohol, or when the alcohol is simply mixed with water, its admixture with some changeable organic substance being an essential condition.

$$C_2H_6O + O_2 = C_2H_4O_2 + H_2O.$$

Alcohol + Oxygen = Acetic acid + Water.

This action, however, can scarcely be considered fermentation, but simply a process of oxidation (decay), the mycoderm acting (1) as a carrier of oxygen to the alcohol, and (2) as the means of bringing the oxygen and the alcohol into actual contact. This action is analogous to that which occurs in the oxidation of alcohol to aldehyde and to acetic acid by spongy platinum.

The active agent, as we have said, of this change is the *mycoderma aceti.*

Thus it would appear that elementary plants have the power of breaking up organic bodies, each little organism having its own special soil on which to work, the products formed being dependent both on the organism and on the soil.

(2.) The Conditions Necessary to Produce Fermentation.

(*a.*) *The presence of a ferment;* that is of a nitrogenous albuminous body in a state of active decomposition. Illustrations of ferments are found in *Emulsin,* the active agent of the bitter almond in converting the amygdalin into hydrocyanic acid, &c. ; in *Myrosin,* a ferment-like substance present in the seeds of the black and white mustard, which converts the myronate of potassium into the oil of mustard (C_3H_5CNS) together with glucose and hydric potassic sulphate ; in *Diastase,* a body found in malt, saliva, &c., by the action of which starch is converted into glucose ; in *Casein,* which in milk induces lactic acid fermentation of the sugar ; and, amongst many other illustrations that might be quoted, in *Yeast,* which is the ordinary ferment employed for setting up alcoholic fermentation.

This last ferment, the ordinary beer yeast, has been specially studied. When the yeast is merely dried at a low temperature, (forming what is called "dried yeast,") its power as a ferment is not impaired, but if the yeast be boiled in water it is then completely destroyed. "German dried yeast," consists of the dried yeast cells produced in the fermentation of rye for making Hollands.

Yeast, however, is a complicated ferment. It consists of two kinds of cells, (1) large round granular cells (*torula cerevisiæ*), and (2) certain oval-shaped cells of a much smaller size (*penicillium glaucum*). If the yeast be mixed with water, and then filtered through paper, the smaller cells pass through with the water, leaving the larger cells on the filter paper. It is found that *the large cells* generate vinous, and *the small cells* lactic fermentation, when they are added respectively to a solution of sugar.

When yeast is added *to a solution of pure sugar* it sets up fermentation, but the yeast-cells are for the most part destroyed as fermentation proceeds. A few fresh yeast-cells may be formed, but if so, it is at the expense of the materials produced by the disintegration of other yeast-cells. Hence, a given quantity of yeast can only convert a limited quantity of *pure* sugar into alcohol. When the yeast is added to a *solution of sugar*, the solution also containing *nitrogen* in some form or another, and *phosphates*, it then not only ferments the sugar, but propagates itself. Under such circumstances the addition of a little yeast, owing to its rapid growth, will convert an almost unlimited amount of sugar into alcohol. Thus the presence of nitrogen and phosphorus in a combined form, are essential conditions for the growth and propagation of yeast-cells.*

In the case of grape-juice no ferment need be added, as, after exposure to the air for an hour, or even less, the vegetable albumen in the juice undergoes decay by oxidation, and acts as a ferment to the sugar.

It has been suggested that certain miasmata act as blood-ferments, and induce the diseases ordinarily known as zymotic (*ζύμη*, ferment) or ferment-diseases.

We have remarked that all ferments contain nitrogen. Nitrogen is an element remarkable for rendering the bodies in which it occurs unstable. The chemical relationships of nitrogen are worthy of note; it stands mid-way in the chemical scale between metals and metalloids, without any great affinity for either the one or the other. It combines both with oxygen and with hydrogen (and indeed with most bodies), but its *direct* union is not easily effected. Hence, its attractions being equally powerful in opposite directions, great instability invariably characterizes the compounds in which it is present.

(*β.*) *A body to ferment.* The sugars (glucoses) are, *par excellence*, the bodies peculiarly liable to ferment. If yeast be added to a solution of gum no action will be apparent, nor will the yeast itself be propagated. The action of yeast, however, is not confined to sugar; for if it be added to a solution of malic acid, succinic, acetic and carbonic acids are formed, although it is to be remarked that in this case the yeast itself does not propagate.

(*γ.*) *The actual contact of the ferment and the body to be fermented.*—The necessity for actual contact was proved by Mitscherlich as follows: A glass tube, the bottom of which consisted merely of a piece of fine filter-paper, was partially immersed in a solution of sugar. The solution rapidly penetrated the pores of the paper, and filled the tube to the level of the external liquid. A small quantity of yeast was then added to the liquid *in the tube*, when the solution contained in the tube, after a short time, commenced fermenting, but there were no signs of fermentation in the solution external to the tube, the piece of bibulous paper stopping the actual contact of the yeast-cells with the external fluid by stopping the passage of the yeast globules, although it did not interfere with the intercommunication of the liquids.

---

* Yeast yields from 6 to 8 per cent. of ash, which consists entirely of alkaline and earthy phosphates. (Mitscherlich.)

(δ.) *A certain temperature.* At 32° F. (0° C.) fermentation is arrested. From 32° F. to 68° F. (0° C. to 20° C.) it gradually increases in intensity with the rise of temperature. From 68° F. to 104° F. (20° C. to 40° C.) it is most active. At 120° F. (49° C.) the process is again stopped. Hence certain times of the year are preferable for brewing (especially the autumn), the temperature at such times falling within the proper limits.

(ϵ.) *The presence of moisture.* Water is necessary to bring the particles into contact. Dry yeast and dry sugar cannot ferment.

We may note, lastly, that *the presence of air* is not necessary for fermentation, provided the previous conditions be fulfilled.

It has nevertheless been proved by Pasteur, that the action of the air in the process of fermentation is not to be disregarded. For it may act either (1) as a carrier of the ferment germs, or (2) as an oxidiser, inducing the decay of certain nitrogenous bodies present in a solution, thereby rendering them capable of acting as ferments.

(1.) If a solution of sugar, no yeast having been added, be exposed to the atmosphere, it becomes loaded before long with the lower forms of organic life, and the solution begins to ferment. If, however, the air, before being allowed to come into contact with the sugar solution, be sterilized, either by passing it through a red-hot tube, or through a tube containing cotton-wool (care being taken that the saccharine liquid itself has been absolutely freed from germs by previous boiling), no fermentation will occur ; but if the dust strained from the air by the cotton-wool be placed in the solution, rapid decomposition of the sugar results.

Hence Pasteur concludes that the air may act as the carrier of the seeds necessary to start fermentation in a solution disposed to ferment.

(2.) In the case of wine juice, which ferments spontaneously, the air is supposed to oxidise the vegetable albumen, which in a decomposed state is capable of acting as a ferment on the sugar.

(3.) The Circumstances Influencing Fermentation.

The following circumstances *prevent* fermentation :—

(α.) *The presence either of an excess of strong mineral acids, or of a trace of free alkali.*

(β.) *The presence of certain salts in the solution*, such as sulphites, $NaCl$, $AgNO_3$, $CuSO_4$, etc.

(γ.) *The presence of certain alkaloids*, such as strychnia, quinia, etc. These do not, however, stop fermentation, if added *after* the process has commenced.

(δ.) *The presence of certain essential oils,* such as kreasote, turpentine, etc.

(ϵ.) *A solution containing more than one-fourth its weight of sugar.* The strength of the sugar solution is important. If it be *too strong,* fermentation is arrested, or rendered imperfect; if it be *too weak*, the action is slow and irregular.

(ζ.) *A solution containing more than* 20 *per cent. of alcohol.* Hence no fermented liquor can contain more than 20 per cent. of alcohol naturally. Anything in excess of this is evidence that spirit has been added (fortification) after the fermentation of the liquid was complete.

Fermentation is influenced by many other causes. Thus—

(1.) *The products formed at different temperatures vary.* Thus, if yeast be made to act at a temperature of 70° F. (21·1° C.) on malic acid, it forms amongst other things succinic acid, whilst at a higher temperature it yields butyric acid.

(2.) *The alteration of pressure.* Fermentation is not stopped by placing the solution in a vacuum, but it is stated that under such circumstances the ratio of the alcohol to the carbonic anhydride formed, is different to that which occurs under ordinary atmospheric pressure, the CO_2 as well as the hydrogen, acetic acid, etc., becoming proportionately greater. (H. Brown.)

(4.) The Theories to Account for Fermentation.

We may note, *First*, that the ferment is destroyed during the fermentative process, the propagation and growth of new buds being due partly to the disintegrated cells that have done their work, but principally to the nitrogenized matters and phosphates present in the solution. *Secondly:* that during the disintegration of the ferment cells, the body undergoing fermentation breaks up into simpler groups.

These being admitted facts, we may now notice the theories to account for the action of the ferment.

(1.) *Berzelius* explained it by the influence of a force which he called *Catalysis,* a word signifying Fermentation. He thus assumed the existence of a new force, but at the same time acknowledged indirectly his inability to perceive, or to detect the force, and the impossibility of explaining its action.

2. *Pasteur's* theory is as follows. The ferment, he considers, grows and multiplies at the expense of the sugar. This act of the ferment in withdrawing from the sugar a portion of its constituent matter, he regards as essential to the process of fermentation, and the primary cause of the sugar itself breaking up into simpler groups.

3. *Liebig* admits that the ferment may multiply at the expense of the sugar, but at the same time refuses to admit that the withdrawal of the matter from the sugar necessary for the propagation of the yeast cells, is the cause of the phenomena of fermentation. He considers that fermentation is due to the active state of change going on within the yeast cell being communicated to the sugar in actual

contact with it, thereby inducing in the sugar the breaking up process that the yeast cell itself is undergoing; in other words, that the disturbance going on in the yeast is mechanically communicated to the sugar, thereby effecting its breaking up and re-arrangement. Hence, according to Liebig, if the yeast grows at the expense of the sugar, it is merely to maintain a supply of the material necessary to keep it in a continuous state of disturbance.

This theory is not unphilosophical although theoretical. That one body in motion may communicate its motion to another body not in motion, thereby overturning the existing equilibrium of that body, is a phenomenon of constant occurrence.

(5.) The Practical Applications of the Process of Fermentation.

(*a.*) *Alcoholic Fermentation.* (1.) *Wine-making.* The expressed grape-juice (the must) is first of all freely exposed to the air. The air decomposes the vegetable albumen of the juice, and this at once acts as a ferment on the grape sugar. If the sugar be in excess and the albumen deficient, we obtain *a sweet wine;* if the sugar be deficient, and the albumen in excess, *a dry wine* results. During fermentation, *argol* (acid potassic tartrate) is deposited, owing to its insolubility in dilute spirit. This circumstance constitutes the superiority of the grape over all other fruits for wine-making—the separation of the acids of other fruits, such as of gooseberries and currants (viz., malic and citric acids) not being effected during fermentation, and their taste consequently requiring to be masked by the addition of an excess of sugar.

The color of red wines is derived from the grape skins. Effervescent wines are bottled before fermentation is complete.

(2.) In *brewing*—the barley has first to be malted. *Malting* consists in setting up germination, by the combined action of air, heat, and moisture on the seed, and then stopping germination by drying the seed at 140° F. (60° C.) The object of this is to convert (by oxidation) the gluten of the seed into *Diastase* (*διάστασις*, decomposition), a peculiar, ferment-like body which has the power of changing the *insoluble* starch of the seed first into dextrin, and finally into *soluble* grape sugar. In nature, this process is necessary in order to supply the germ with its first food, which must be presented to it in a soluble form. The malt is then bruised, treated with water, and the liquid set aside for some time—any unconverted starch in the malt being thus brought into contact with the diastase, and its complete conversion into sugar effected. One part of diastase will convert 2,000 parts of starch into grape sugar, but the power of the diastase is itself exhausted during the process. The malt-mash is now strained, the clear liquor constituting what is called "the wort," and the undissolved portion "brewer's grains." The clear liquor is now boiled with hops, the bitter resinous principle of which (lupuline) not only gives flavour to the beer, but prevents it undergoing acetous fermentation. It is finally mixed with yeast, when the beer "works," that is "ferments," the sugar splitting up into alcohol and carbonic acid.

The malt used in the manufacture of porter is partially caramelized or "high dried."

(3.) In *spirit-making*, the distiller prepares a wort or "*wash*," like the brewer, with this exception, that he mixes 4 parts of unmalted with 1 part of malted grain, the diastase of the latter being sufficient to convert the whole of the starch of the former into sugar. Thus, much of the labour and expense of malting is avoided. Moreover the distiller has no need to add hops to his wort, nor to consider the details of fermentation as the brewer is compelled to do, except that it should be as complete as possible. A large quantity of spirit is prepared from potatoes and also from corn, the starch of which may be converted into sugar by admixture with a little malt. In both cases, however, a small quantity of a very acrid oil (fusel oil) accompanies the ethylic alcohol, and this it is the duty of the rectifier to separate by careful distillation, the fusel oil being less volatile than the alcohol.

(4.) *In bread-making*, a little yeast is mixed with the dough, the object being to render the bread light and spongy. The sugar of the flour ferments, generates carbonic anhydride, which causes the bread to "rise," the spirit formed during "the working," escaping when the bread is baked.

Ammonic carbonate, sodium carbonate and hydrochloric acid, and lastly a stream of pure carbonic acid (Dauglish), have been suggested in bread-making in the place of yeast. In ancient days, a piece of dough in a state of incipient putrefaction (leaven) was used as a ferment.

(β.) *The lactic fermentation.*—This is seen in the ordinary decomposition of milk into curds and whey. *Koumiss* is fermented mare's milk. It is a spirituous liquor.

(γ.) *The acetous fermentation.*—Illustrations of "acetification" may be noticed in beer turning sour, the acidity being due to acetic acid; and also in what is called the "quick vinegar process." This latter consists in allowing a heated mixture of alcohol and yeast (the yeast being added to supply the necessary nitrogenous matter) to trickle over wood shavings soaked in vinegar, the wood shavings serving as points of attachment for the mycoderm. It is essential that the supply of air be very free. If the supply of air be *limited*, aldehyde is formed, and much loss of vinegar results :—

$$\underset{\text{Alcohol}}{C_2H_6O} + \underset{\text{Oxygen}}{O} = \underset{\text{Aldehyde}}{C_2H_4O} + \underset{\text{Water};}{H_2O;}$$

but if the supply of air be *free*, aldehyde is not formed, or if it be formed, is immediately oxidised :—

$$\underset{\text{Alcohol}}{C_2H_6O} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Acetic acid}}{C_2H_4O_2} + \underset{\text{Water.}}{H_2O.}$$

The *French wine-vinegar* is prepared from light wines, by first mixing them with a little boiling vinegar, and then allowing the mixture to trickle over wood shavings into casks.

The *English malt vinegar* is prepared from an infusion of malt, which is allowed to undergo both the alcoholic and the acetous fermentation. Commercial vinegar may by law contain the thousandth part of its volume of sulphuric acid, for the purpose of preventing its turning mouldy.

II. PUTREFACTION.

Definition.—A spontaneous change common to all nitrogenised organic bodies when exposed to the air, whereby they are resolved into new and simpler products. The action is accompanied by the evolution of unpleasant gases, which are for the most part compounds of sulphur and phosphorus.

It *differs from fermentation*, in that *unpleasant* products are evolved, as, *e.g.*, in the decomposition of a dead body. Moreover, a putrescible body is always a nitrogenised body, which at a certain temperature in contact with air and moisture, decomposes, and then becomes capable of acting as a ferment.

It *differs from eremacausis* or *decay* in that it is not oxidation, although air is necessary in the first instance to start the action. Modern investigations lead us to believe that the air may be the carrier of spores or ova, having the power of inducing the change. This is assumed because a body liable to putrefaction, does not putrefy if it be boiled in a flask, and when boiling, the neck of the flask plugged with cotton wool. Nevertheless, we see *a relationship between eremacausis, putrefaction and fermentation.* Putrefaction is commenced, like decay or eremacausis, by the action of the air, whilst the putrescent body is capable of inducing fermentation in fermentable solutions. Moreover, like fermentation, putrefaction is always accompanied by the development of certain minute living organisms, fungi and infusoria.

(1.) The Conditions Necessary for Putrefaction.

(*a.*) *Air.*—The presence of air is essential only at the commencement of the process, and not after putrefaction has fairly commenced. Its progress is then independent of any aid external to itself. Thus fruits and meats are preserved in sealed air-tight tins.

(*β.*) *Moisture.*—A perfectly dry body does not putrefy. Thus vegetables when perfectly dry may be preserved for a considerable time (Masson's patent). The preservative action of sugar and salt has been ascribed by some to their attraction for moisture, and their power of withdrawing it from the putrescible body.

(γ.) *A temperature between* 40° *and* 200° F. (4·5° *and* 93·5° C.). Cold prevents putrefaction by inducing cohesion. Thus fish are preserved in ice. The stories of bodies of men and animals having been preserved in the ice of polar regions for many years are numberless. Warmth destroys cohesion, and thus aids putrefaction, whilst too great a heat destroys the body by burning it up.

(2.) Means of Preventing Putrefaction.

By the general term "disinfectant" we include antiseptics and deodorizers.

An *antiseptic* is an agent that prevents putrefaction, and entirely stops the evolution of offensive gases.

A *deodorizer* is an agent that either absorbs or destroys offensive gases, but does not prevent their formation—in other words, does not prevent putrefaction.

Disinfectants are of two kinds—*natural* and *artificial*:—

1. *Natural disinfectants*—

(α.) The *Atmosphere*. This acts (1) mechanically by its power of removing foul vapors and other matters, and (2) chemically by effecting their oxidation.

(β.) *Water*. Its action is chiefly *mechanical*. In a river, during its flow, the organic matter becomes disintegrated, rapid purification by the oxygen in solution in the water resulting. Every shower of rain purifies the air. Besides cleansing powers, water, by reason of its endosmic action, is inimical to the corpuscular structures of many specific contagia, destroying their vitality by bursting their cell-like envelopes.

(γ.) *Soil*. The power of soil is manifested in our graveyards. Owing to its porosity it effects the oxidation of decomposing matter. In the presence of alkalies, ammonia is rapidly oxidized to nitric acid, the ferric oxide present acting as a purveyor of atmospheric oxygen.

(δ.) *Light*.

(ε.) *Heat and Cold*. Vaccine matter loses its power at 140° F. (60° C.) and the virus of scarlet fever at 204° F. (95·5° C.). The common vibrio is destroyed at 300° F. (149° C.), and the black vibrio at 400° F. (204·5° C.). Others assert that none of the lower organisms will bear a temperature of 266° F. (130° C.) in air, or of 230° F. (110° C.) in water. [Note.—A heat of 250° F. (121° C.), aided by a jet of steam, may be safely used in disinfecting textile fabrics.]

2. *Artificial disinfectants*.

(α.) *Mineral acids*; such as sulphurous, nitric, hydrochloric, sulphuric and chromic acids. In this order, they have the power of stopping the development of infusoria in organic solutions, sulphurous acid being the least, and chromic acid the most powerful.

(β.) *Organic acids;* such as carbolic, cresylic, acetic, picric, benzoic acids; benzoic being the most powerful, and acetic the least so.

(γ.) *Alkalies.* Lime, potash, soda, and ammonia are only active disinfectants when used in a concentrated form. Lime is used in stables for the purpose of assisting the oxidation of the organic matter.

(δ.) The *haloids.* Iodine acts as a mild, and chlorine as a powerful, disinfectant. Chloride of soda ("Labarraque's Liquid"); chloride of zinc ("Sir Wm. Burnett's Fluid"), the action of which is due to its power of coagulating albumen and of absorbing ammonia and sulphuretted hydrogen; chloride of aluminium ("chloralum"), which is neither an aërial disinfectant nor possesses the slightest deodorising power; common salt and other chlorides are also frequently used.

(ϵ.) *Mineral Sulphates.* Sulphates of zinc, of iron ("Mudie's Disinfectant"), of alumina and of copper act as disinfectants, the action being dependent on their power of coagulating and destroying living organisms, and of neutralizing offensive miasms.

(ζ.) *Potassic Permanganate and Chlorozone.* These destroy *dead* organic matter, but have very little action, so far as we know, on *living* organic matter.

(η.) *Volatile Oils; Camphor; Turpentine,* etc. These hinder the development of fungi and animalcules, and are said to generate ozone. It was believed in former times that aromatic herbs about a house warded off pestilence.

(θ.) *Charcoal and other porous bodies.* The action of such bodies is due to their power of absorbing noxious gases, and effecting their destruction by bringing them into contact with condensed atmospheric oxygen. But it must be remembered that it is essential for the action of charcoal that there should be a free supply of atmospheric air.

Note, as regards disinfectants, the following practical hints:—

1. Certain disinfectants, such as chlorine, chloride of lime, sulphurous acid, carbolic acid, and volatile oils, are *aërial* disinfectants, and may be used for the purification of air; whilst others, such as chloralum, permanganate of potash, chlorozone, the mineral sulphates, chloride of zinc, etc. are useless for the purpose of purifying the air of a sick room, inasmuch as they are not volatile.

2. Neither chlorine, hypochlorous acid, carbolic acid, nor sulphurous acid can be used to disinfect a chamber when a person is living in it, the quantity required efficiently to effect this object rendering the atmosphere absolutely irrespirable. Hence perfect disinfection is only possible when a room is vacated. The combustion of 1½ ozs. of sulphur to every 100 cubic feet of space in a room, is necessary to effect good disinfection.

3. Chloride of zinc and strong carbolic acid being corrosive bodies, should not be used for the disinfection of textile fabrics, but are valuable for such purposes as the disinfection of fæcal matter, etc.

4. In disinfecting clothing *at the sick house,* boil the articles in water

and then steep them in a solution of carbolic acid (℥iv. to 1 gallon), To disinfect clothes completely, however, they should be submitted first to sulphurous acid, and then for at least six hours to a temperature of from 240° to 250° F. (115·5° to 121° C.).

5. In disinfecting stables, cattle lairs, slaughter-houses, etc., there is nothing better than lime, on account of its detergent as well as of its disinfecting properties.

6. In the treatment of sewage, lime and alumina act as excellent defecatory and precipitating agents.

III. EREMACAUSIS (*ἤρεμος* gentle, *καῦσις* combustion) *Decay.*

Definition.—The decomposition of moist organic bodies *by oxidation* into simpler groups, or, in other words, the *slow burning* of organic bodies. This action is unaccompanied by any sensible elevation of temperature. It is seen in the *decay of wood,* where a brown powder (ulmin or humus) is left, the hydrogen oxidizing more readily than the carbon ; also in *the drying of oils,* solidification being attended with the absorption of oxygen (which has been known to be so rapid that combustion has resulted) ; also in *the formation of acetic acid* from alcohol; and in many other processes.

(1.) The Conditions necessary for Decay.

(*a.*) *The free access of atmospheric air.*—There are reasons to believe that the active agent in inducing eremacausis is ozone (see page 77). Thus bodies are found to be specially prone to decay after a thunderstorm, during which ozone is largely developed. Ozone, however, never accumulates in the air, but is used as fast as formed to oxidize organic matter and vapours of organic origin. It is however more than probable that ordinary oxygen can carry on the process or decay when once the action has been started—although it must be remembered that the development of ozone itself, is a consequence or result of eremacausis, the decaying body furnishing the active agent necessary for its further destruction.

(*β.*) *The presence of moisture.*—Perfect dryness suspends decay, as it does fermentation and putrefaction. A body which is incapable of absorbing oxygen when dry will often do so when moist. Thus in the "grass bleaching" of calicoes, where oxidation (eremacausis) only is relied upon for effecting the destruction of the coloring matters (a part of the cotton itself being oxidized at the same time), it is found to be necessary to keep the fabrics moistened with water.

Thus again, in the formation of coal and peat, the presence of moisture is an essential condition.

(*γ.*) *A certain temperature.*—Cold by increasing cohesion interferes with decay ; at the freezing point 32° F. (0° C.) decay is arrested. Warmth by its opposite action effects decay.

(2.) The Circumstances Influencing Eremacausis.

(*a.*) The action *is promoted by warmth.*

(*β.*) The action *is promoted by the presence of alkalies.* Thus in the formation of nitres the oxidation of ammonia takes place in the presence of a powerful base (*see* page 321).

(*γ.*) The action *is checked by certain antiseptic salts.*

(*δ.*) The action *is promoted by the contact of an eremacausing body.* Just as one body on fire is capable of inflaming a body not on fire, so a body undergoing decay can by contact, produce decay in a substance liable to it. To prevent this contact oranges are packed in paper, etc., etc.

(*ε.*) The action *is promoted by the presence of porous substances, such as charcoal,* etc., whereby the oxygen is absorbed and condensed, and its actual contact with the body effected.

(*ζ.*) The action is promoted by *an excess* of ozone in the atmosphere, such as occurs under certain atmospheric conditions.

(B.) ARTIFICIAL DECOMPOSITION.

I. Action of Heat on Organic Bodies.

Heat decomposes *all organic matter*, whereby new products (called *products of destructive distillation*) are formed. These, on cooling, never resolve themselves into the same states of combination in which they existed originally in the organic body. The more complicated the organic body, the more easily is it decomposed by heat.

Heat acts *on many inorganic* compounds; sometimes these products do not re-combine on cooling, but most often the action of the heat is reversed when the temperature is lowered. For example, calcium hydrate (CaH_2O_2) by heat is resolved into lime (CaO) and water (H_2O), but these on cooling again combine to form calcium hydrate.

Heated *in the open air,* some organic bodies sublime, *e.g.*, benzoic acid; others partly decompose, *e.g.*, gallic acid ($C_7H_6O_5$) yields pyrogallic acid ($C_6H_6O_3$) and carbonic anhydride; others simply burn (their carbon forming carbonic acid, and their hydrogen water), by combining either with their own oxygen or with the oxygen of the air.

When organic bodies are heated *in closed vessels,* the process is known as "destructive distillation." Simpler and more stable compounds are formed, a residue of carbon mixed with the incombustible ash remaining in the retort.

The products of destructive distillation vary with the body operated on, and with the temperature employed:—

(1.) This may be noticed, for example, *in the distillation of non-nitrogenised bodies, such as wood*:—

(*a.*) *At the lowest temperature,* compounds are given off containing much oxygen, such as water, acetic acid, carbonic anhydride, etc.

(β.) *At a higher temperature,* the compounds evolved contain less oxygen, such as carbonic oxide, wood spirit, kreasote, etc.

(γ.) *At a still higher temperature,* various hydrocarbons distil over, such as toluene, xylene, and the different forms of paraffin, etc.; whilst

(δ.) *At a temperature approaching redness,* pure hydrogen predominates.

Some of the Products of the Action of Heat on Coal.

COMPOUNDS, Etc.	Formula.	Molecular Weight.	Specific Gravity.	Specific Gravity of Gas or Vapor.	Boiling point.		Fusing point.	
					° F.	° C.	° F.	°
(A) COAL GAS.								
Marsh gas (Methane)	CH_4	16		0·559				
Olefiant gas (Ethene)	C_2H_4	28						
Acetylene (Ethine)	C_2H_2	26		0·92				
Hydrogen	H	1		0·0693				
Carbonic oxide	CO	28		0·973				
Nitrogen	N	14						
Vapors of various hydrocarbons								
Vapor of carbon disulphide	CS_2	76	1·272	2·67	109·4	43		
Sulphuretted hydrogen	H_2S	34		1·171				
Carbonic acid	CO_2	44		1·524				
Tar and volatile oils								
Ammonia	NH_3	17						
(B) AMMONIA WATER.								
Ammonium carbonate								
,, sulphide								
,, cyanide								
,, sulphocyanide								
(C) COAL TAR.								
Neutral hydrocarbons.								
(*Liquid.*)								
Benzene	C_6H_6	78	0·880	2·77	177	80·6		
Toluene	C_7H_8	92	0·872	0·87	230	110		
Xylene	C_8H_{10}	106	0·865	0·87	284			
Cumene	C_9H_{12}	120	0·870	0·85	338			
(*Solid.*)								
Naphthalene	$C_{10}H_8$	128	1·153	4·528	413·6	212	174	
Anthracene	$C_{14}H_{10}$	178	1·147	6·741	680	360	416	
Chrysene	$C_{18}H_{12}$	228			824	440	450	
Pyrene	$C_{16}H_{10}$	202			700	382	288	
Phenanthrene	$C_{14}H_{10}$	178			644	340	208	
Alkaline products.								
Ammonia	NH_3	17						
Aniline	C_6H_7N	93	1·02	3·21	360	182		
Picoline	C_6H_7N	93	0·961	3·29	271	135		
Quinoline (leucoline)	C_9H_7N	129	1·081	4·519	462	239		
Pyridine	C_5H_5N	79	0·980	2·92	242	117		
Acid products.								
Carbolic acid (phenol)	C_6H_6O	94	1·065		370	187	95	
Cresylic acid (cresol)	C_7H_8O	108	1·050		397			
Acetic acid	$C_2H_4O_2$	60	1·06		243	117		

(2.) *In the case of nitrogenised bodies, such as coal,* a part of the nitrogen is evolved as ammonia and basic bodies allied to it (such as aniline (C_6H_7N), quinoline, pyridine, etc.), and also as cyanogen: whilst a part of the nitrogen remains in the still, together with the carbonaceous residue.

It will be convenient here to notice the products of the destructive distillation of *Coal* and of *Wood,* the former serving as an illustration of the action of heat on a nitrogenized body, and the latter of heat on a non-nitrogenized body.

(1.) The Products of the Distillation of Coal (or other nitrogenized substances).

The coal is distilled in retorts, connected with which are iron delivery pipes. These ascend perpendicularly for a few feet, and then curving round, dip below the liquid contents of a large horizontal pipe, called "the hydraulic main," which acts both as a water valve, and as a receiver for the delivery pipes from the retorts. This pipe receives the tar and the gas liquor, through which the impure gas bubbles. Thus we obtain the coke in the retort, and the gas, the gas-water, and the coal tar, as the products of the distillation.

1. Coal Gas.—[A ton of coal yields in practice from 9,500 to 11,000 cubic feet of gas.]

Coal gas is, as the table shows, a compound of a variety of gases and vapors. The relative proportion of the several constituents is influenced by the temperature at which the gas is prepared. The heat should always be at its maximum at the commencement of the operation. (*a.*) If it be *too high,* the heat of the retort decomposes the marsh and olefiant gases and hydrocarbon vapors, carbon being deposited in the retort (*gas carbon*). An excess of hydrogen therefore escapes, and the illuminating power of the gas suffers in consequence. Hence the use of *exhausters* in order to hasten the exit of the gas from the retorts. Moreover, at a high temperature, bisulphide of carbon is formed, the complete removal of which from the gas is practically impossible. (*β.*) If the heat be *too low,* the gas contains too great an excess of solid and liquid hydrocarbons, which tend to block up the tubes. These facts are well shown in a table (from Bloxam), illustrating the composition of coal gas at different periods of its distillation:—

In 100 volumes.	1st hour.	5th hour.	10th hour.
Olefiant gas and volatile hydrocarbons ..	13·0	7·0	0·0
Marsh gas	82·5	56 0	20·0
Carbonic oxide	3·2	11·0	10·0
Hydrogen	0·0	21·3	60·0
Nitrogen	1·3	4·7	10·0

The increase of the carbonic oxide at the fifth hour may arise from the carbon decomposing the H_2O at high temperatures, and the increase of the nitrogen from the decomposition of the ammonia.

The gas as it leaves the hydraulic main needs *purification.* This is effected by various contrivances :—

(1.) *The Condensers* (*refrigerators*) consist of a series of bent iron pipes through which the gas is made to travel. By thus exposing a large surface of the gas to the air, any tar or ammonia liquor that escapes the hydraulic main, owing to the gas being superheated, will be condensed.

(2.) *The Scrubber* is a tower filled with wet coke or other material. By this means the removal of the ammonia from the gas is effected. [The evil of the scrubber is that it diminishes the illuminating power of the gas, by removing, at the same time as the ammonia, a portion of the more condensable hydro-carbons.]

(3.) *The Purifiers.*—The object of these is to remove the carbonic anhydride (which is said to decrease the illuminating power of the gas) and also the sulphuretted hydrogen, and other sulphur impurities, such as CS_2, COS, etc.

To get rid of carbonic acid and sulphuretted hydrogen (and also of sulphocyanogen, cyanogen, etc.), purifiers are employed containing either—

(*a.*) *Lime,* a carbonate and a sulphide of lime being formed, or,

(*β.*) *Oxide of iron* (Fe_2O_3) (mixed with sawdust to prevent caking). Oxide removes sulphuretted hydrogen and hydrocyanic acid only from the gas. (Thus, $Fe_2O_3 + 3H_2S = 2FeS + S + 3H_2O$. With hydrocyanic acid, Prussian blue or some similar compound is formed.)

The great advantage of oxide is the ease with which the iron sulphide can be again converted into oxide (revivified), by exposure to air. The oxide may be used for gas purification over and over again, the sulphur collecting in the mass, until finally, after repeated revivifications, the percentage of sulphur present in the oxide renders it of commercial value for the manufacture of oil of vitriol (*see* p. 181).

To get rid of sulphur impurities other than the sulphuretted hydrogen, many processes have been suggested, of which the following are the most important :—

(*a.*) *Sulphide of lime.*

(*β.*) *By washing with the ammoniacal liquor.*

(*γ.*) *By the action of steam at a high temperature,* whereby CO_2 and H_2S are formed, both of which are easily removed from the gas :—

$$\underset{\text{Carbonic disulphide}}{CS_2} + \underset{\text{Water}}{2H_2O} = \underset{\text{Carbonic anhydride}}{CO_2} + \underset{\text{Sulphuretted hydrogen.}}{2H_2S.}$$

(δ.) *By red-hot lime:—*

CS_2	+	$3CaO$	=	$CaCO_3$	+	$2CaS$.
Carbonic disulphide	+	Lime	=	Calcic carbonate	+	Calcic sulphide.

(ϵ.) *By a solution of lead oxide in caustic soda:—*

CS_2	+	$2PbO$	+	$2NaHO$	=	$2PbS$	+	Na_2CO_3	+	H_2O.
Carbonic disulphide	+	Lead oxide	+	Sodic hydrate	=	Plumbic sulphide	+	Sodic carbonate	+	Water.

Finally the gas passes to the gasometer.

It has been suggested to mix a certain small percentage (2·5 per cent.) of lime with the coal, whereby the sulphur products evolved in the gas are considerably reduced.

(2.) **The Gas Liquor.**—From this liquor containing numerous ammoniacal salts (chiefly the carbonate, sulphide, cyanide and sulpho-cyanide), the various salts of ammonia in commerce are obtained, either by the direct action of acids on the liquor, or by setting free ammonia by distillation with lime.

(3.) **The Coal Tar.**—This is distilled in iron retorts.

The tar contains three sets of products: (α) *those volatile at a low temperature;* (β) *those volatile at a high temperature*; (γ) *those not volatile at the temperature of the still.*

(α.) *Those volatile at a low temperature.*—The distillate which in the first instance comes over with the steam is called *light oil*, from its having a less specific gravity than, and consequently floating on, the condensed water. Every 100 parts of tar yield about 10 per cent. of light oil.

The light oil contains benzene, toluene, xylene, cymene, etc., contaminated with more or less dead oil. The light oil is again distilled, the distillate forming what is called *coal naphtha*, a quantity of 'heavy oil' remaining in the retort. The coal naphtha is purified by shaking it up, first with sulphuric acid, whereby basic substances are removed, then with a dilute solution of potash to separate carbolic acid, etc., and finally with water. When decanted from the water, it forms "rectified coal naphtha." This composite liquid may be separated into its various constituents by fractional distillation:—

From 175° to 180° F. (79·4° to 82·2° C.) it yields pure benzene.
„ 180° „ 230° F. (82·2° „ 110° C.) „ „ ?
„ 230° „ 235° F. (110° „ 113° C.) „ „ toluene.
„ 284° „ 293° F. (140° „ 145° C.) „ „ xylene.
„ 336° „ 342° F. (168·9° „ 172° C.) „ „ cymene.

Commercially that portion which distils over between 175° and 250° F. (79·5° and 121·1° C.), is designated and sold as benzol or benzene.

(β.) *Those volatile at a high temperature.*—These constitute the liquid called "dead oil," or "yellow oil," from its peculiar color, or "heavy oil," from its being heavier than, and therefore sinking in, water. The last portions that distil over become nearly solid on cooling. Every 100 parts of tar yield about 25 per cent. of dead oil.

Dead oil contains carbolic acid, naphthalene, anthracene, aniline, quinoline, etc.

Amongst the *first* products of the distillation of dead oil, is *carbolic acid* (C_6H_6O). It comes over chiefly between 300° and 400° F. (149° and 250° C.), and is largely used for creosoting timber.

Amongst the *last* products of tar distillation is *anthracene* ($C_{14}H_{10}$), a body of great commercial value in the manufacture of artificial alizarine. The first portion of the anthracene that distils over, is mixed with naphthalene ($C_{10}H_8$), and the last with chrysene ($C_{18}H_{12}$). Anthracene is purified in the first instance by re-distillation, the first and last portions being rejected. The intermediate portion is purified by crystallizing either from its solution in alcohol, or in coal oils boiling between 212° and 248° F. (100° and 120° C.).

(γ.) *Those not volatile.*—These constitute the black residue in the retort called *pitch*. It is used in the preparation of Brunswick black, asphalt, etc.

By the action of heat on horny matters, similar products to those already described are formed, the ammonia (hartshorn) being produced in great quantity, owing to the richness of horn in nitrogen.

(2.) The Products of the Distillation of Wood (or other non-nitrogenized substances).

The following exhibits the difference in the ultimate chemical composition of coal and wood :—

Per 100 parts.	Carbon.	Hydrogen.	Nitrogen.	Oxygen.
Bituminous coal..	79·5	5·5	1·9	13·1
Wood (dried oak)	51·6	5·7	0·2	42·5

We note, therefore :—

(1.) That in wood there is about one-third less carbon than in coal.

(2.) That in wood there is a mere trace of nitrogen (0·2 per cent.), whilst in coal the quantity of nitrogen is considerable (1·9 per cent.).

(3.) That in wood there is more than three times as much oxygen as in coal.

(4.) That the proportion of hydrogen in both is about the same.

From this we should expect that in the destructive distillation of wood compared with that of coal :—

(1.) The gases evolved would be less illuminating.

(2.) The nitrogenized products, such as ammonia, etc., produced, will be less in quantity.

(3.) A great excess of oxidized products, such as water, carbonic acid and oxide, acetic acid, etc., will be formed.

The wood, contained in an iron cage, is placed in a retort and heated. Wood charcoal remains in the retort, and the products of the distillation are as follows :—

Wood Tar.

Solids.

Paraffin	C_nH_{2n+2}	Pyrene	$C_{16}H_{10}$
Naphthalene	$C_{10}H_8$	Chrysene	$C_{18}H_{12}$
Cedriret (Coerulignone)	$C_{16}H_{16}O_6$	Resin	

Liquids.

Toluene	C_7H_8	Pyroligneous or acetic acid	$C_2H_4O_2$
Xylene	C_8H_{10}	Wood naphtha	CH_4O
Cymene	$C_{10}H_{14}$	Acetate of methyl	$CH_3.C_2H_3O_2$
Kreasote	C_7H_8O	Formate of methyl	$CH_3.CHO_2$
Kapnomor	$C_{10}H_{11}O$	Acetone	C_3H_6O
Eupione	C_5H_{12}	Water	

Gases.

Marsh gas	CH_4
Carbonic oxide	CO
Carbonic acid	CO_2

The wood generally employed is what is known as "cord wood," *i.e.*, the trimmings of trees too small for timber. The wood is usually weathered from six months to a year before being distilled, in order to get rid of some of the moisture. The wood of the willow and alder is commonly sorted out and carefully barked, the charcoal obtained from these being found in practice to be that best suited for gunpowder.

The wood, placed in iron boxes, is wheeled into an oven, usually constructed of a size sufficient to receive about 30 cwt. of wood. This done, the door of the oven is securely luted on. The ovens are so constructed that the fire plays around the oven, without coming into direct contact with the wood. An iron pipe, connected with the oven, conveys the distillate from the wood through a cold-water condenser, the condensed liquid being received into a closed wooden trough. This trough requires to be properly and efficiently ventilated to prevent accident, the condensable gases either being allowed to escape or else utilized as a source of heat.

The condensed liquid distillate (equal to about 130 gallons per ton of wood carbonised) is then conveyed into a large tank (sump), where the tar sinks to the bottom, leaving a more or less clear fluid floating upon it. The tar is pumped from the tank into the tar still, whilst the supernatant acid liquid is run into large wooden tanks.

This acid liquor (consisting of wood spirit, pyroligneous acid, etc.) is now thoroughly mixed with lime in the proportion of about 3 cwt. of lime to 1,000 gallons of liquor. This mixture is allowed to rest for some six or eight hours, a quantity of impurities subsiding with the excess of lime. The clear liquid is now pumped into an iron still, holding from 700 to 800 gallons, and heated by a steam coil; the condensed product from this still, after successive distillations, constituting "*methylic alcohol*," or the "*miscible naphtha*" of commerce. The residue in the retort (a solution of pyrolignate of lime) is now drawn off and evaporated to dryness in open pans, the waste heat of the ovens being usually employed for the purpose. This product is sold as crude "*acetate of lime*." The yield of crude acetate is about 140 lbs. per ton of wood carbonised. It commonly contains about 73 per cent. of anhydrous lime acetate.

The tar still, which is usually constructed of a size to hold about 800 gallons, is heated by a naked fire, the distillation of each charge occupying about seventy-two hours. The first distillate that comes over constitutes "solvent naphtha" (not to be confounded with the *miscible* naphtha or methylic alcohol). This, when re-distilled, is sold to the varnish makers. When all the naphtha has come over (the distillate being tested from time to time by noting its inflammability) the next two distillates of the tar—first a watery fluid (practically pyroligneous acid), and afterwards an oily liquid—are conveyed into the tank which receives the liquid distillate from the wood, and are treated along with it. The residue of the tar still ("*pitch*") is allowed to cool in the retort for about twelve hours, and is then run off into the pitch house, which should be an hermetically sealed chamber. Here it remains until it is perfectly cold and solid, the time required for perfect cooling being about forty-eight hours.

Every ton of wood carbonized yields about 20 gallons of tar. Every 800 gallons of tar (a charge) yields about 36 gallons of crude solvent naphtha, the purified naphtha being about two-thirds of the crude naphtha. About one ton of pitch is obtained from every 800 gallons of tar distilled.

The distillation of the wood being complete (the time occupied in such distillation varying from eighteen to twenty-four hours), the iron boxes are withdrawn from the oven and immediately closed with iron lids carefully luted in order to prevent the slightest contact of air during the cooling of the charcoal. The process of cooling occupies about twenty-four hours.

II. Action of Acids on Organic Matters.

(1.) *Sulphuric Acid.*—This acts on organic bodies in different ways, as follows:—

(*a*.) It may combine with the organic body. *Examples:*—Organic bases become sulphates. Alcohol (C_2H_6O) becomes sulphovinic acid or acid-ethylic-sulphate (C_2H_5,HSO_4). Benzoic acid ($C_7H_6O_2$) becomes sulpho-benzoic acid ($C_7H_6O_2,SO_3$). Benzol (C_6H_6) becomes sulpho-benzolic acid (C_6H_6,SO_3). Glycerine ($C_3H_8O_3$) becomes sulpho-glyceric acid ($C_3H_8O_3,SO_3$).

(β.) It may decompose the organic body. *Examples*:—Oxalic acid ($C_2H_2O_4 = CO_2 + CO + H_2O$); formic acid ($CH_2O_2 = CO + H_2O$), etc.

(γ.) It may abstract the elements of water from the organic body. *Examples*:—Thus sugar is carbonized by it. Alcohol (C_2H_6O) becomes ether ($C_4H_{10}O$).

(δ.) It may introduce the elements of water into the organic body. *Examples*:—Dextrine ($C_6H_{10}O_5$) becomes glucose ($C_6H_{12}O_6$).

(ε.) It may dissolve the organic body and effect an alteration in its color. *Example*:—Salicine is turned of a bright red color by the action of the acid.

(2.) *Nitric Acid.* With some organic bodies (as morphia) nitric acid produces a deep red color. The strong acid in many cases effects the complete destruction of the substance on which it acts. For example, sugar is broken up into water and carbonic acid. The chemical effects of the dilute acid on organic bodies vary as follows:—

(α.) It may combine with the organic body. *Examples*:—With basic bodies it forms salts. Ethylamine (C_2H_7N) becomes ethylamine nitrate (C_2H_7N,HNO_3).

(β.) It may effect the oxidation of the organic body. *Examples*:—Sugar ($C_{12}H_{22}O_{11}$) and starch ($C_6H_{10}O_5$) form oxalic acid ($C_2H_2O_4$); gum ($C_{12}H_{22}O_{11}$) forms mucic acid ($C_6H_{10}O_8$).

(γ.) It may form substitution products with the organic body. Thus, nitryl (NO_2) may be substituted for hydrogen, forming nitro-compounds, which are generally explosive. *Examples*:—Benzene (C_6H_6) becomes nitro-benzene ($C_6H_5(NO_2)$); cellulin ($C_6H_{10}O_5$) becomes guncotton ($C_6H_7(NO_2)_3O_5$); glycerine ($C_3H_8O_3$) becomes nitro-glycerine ($C_3H_5(NO_2)_3O_3$).

(3.) *The Haloid Acids* (HCl; HBr; HI).

(α.) These acids may *combine with the organic body*, as in the case of the alkaloids, the compound ammonias, and various unsaturated compounds. Examples: *Ethylamine* (C_2H_7N) becomes ethylammonic chloride (C_2H_7N,HCl); *turpentine* ($C_{10}H_{16}$) becomes hydrochlorate of dadyle, or artificial camphor ($C_{10}H_{16}.HCl$). (The same change occurs by the action of HCl on most essential oils.) *Fumaric acid* ($C_4H_4O_4$) becomes bromo-succinic acid ($C_4H_4O_4,HBr$); *ethylene* (C_2H_4) becomes mono-iodo-ethane (C_2H_4,HI); *hydrocyanic acid* (HCN) becomes hydriodate of formylamine (HCN,HI).

(β.) The substitution of the chlorine, bromine, or iodine of the acid for the group $(HO)'$ may result. This happens more particularly in the case of the alcohols and oxy-acids. *Examples*:—Alcohol ($C_2H_5(HO)$) becomes ethylic iodide (C_2H_5I); oxy-proprionic acid ($C_3H_5(HO)O_2$) becomes bromo-proprionic acid ($C_3H_5BrO_2$).

[In the case of hydriodic acid, it effects the immediate decomposition of the iodine substitution compounds, the iodine being replaced by hydrogen. Thus hydriodic acid is a powerful reducing agent, for it first of all replaces HO by I, and then instantly replaces the I by H.]

(4.) *Phosphoric Acid.*—The anhydride acts as a dehydrating agent. *Example :*—Glycerine ($C_3H_8O_3$) becomes acrolein (C_3H_4O).

III. Action of the Fixed Alkaline Hydrates on Organic Bodies.

(1.) They may combine with the organic body, as, *e.g.*, where salts are formed with organic acids, etc. *Examples :*—Potassic acetate. Camphor ($C_{10}H_{16}O$)+KHO forms potassic campholate ($C_{10}H_{17}KO_2$).

(2.) They may act as oxidising agents, forming acids, with the disengagement of hydrogen. *Example :*—Acetic acid is formed by the action of potassic hydrate on alcohol :—

$$C_2H_6O + KHO = KC_2H_3O_2 + 2H_2.$$

Alcohol + Potassic hydrate = Potassic acetate + Hydrogen.

If the organic body be a nitrogenised body, the nascent hydrogen combines with the nitrogen to form ammonia.

(3.) On chlorine, or on a haloid substitution product, alkalies may effect (α) the replacement of the halogen by the group (HO), or (β) remove the halogen in part or wholly from the compound :—

$$(\alpha.)\ C_2H_5Cl + KHO = KCl + C_2H_5(HO).$$

Ethylic chloride + Potassic hydrate = Potassic chloride + Alcohol.

$$(\beta.)\ C_2H_3Br + KHO = KBr + H_2O + C_2H_2.$$

Bromethylene + Potassic hydrate = Potassic bromide + Water + Acetylene.

(4.) The amides (that is, compounds of amidogen $(NH_2)'$ with an acid radical,) are decomposed by the alkaline hydrates, their nitrogen being evolved as ammonia, whilst the metal (K or Na) forms a salt with the corresponding acid. *Example :*—Acetamide (NH_2,C_2H_3O) becomes ammonia (NH_3) and potassic acetate (KO,C_2H_3O).

IV. Action of Alkaline Carbonates on Organic Matter.

When an organic body containing nitrogen is fused with an alkaline carbonate, carbonic oxide is evolved, cyanogen (as a cyanide of the metal,) being formed. Thus—

$$K_2CO_3 + C_4 + N_2 = 2KCN + 3CO.$$

Potassic carbonate + Carbon + Nitrogen = Potassic cyanide + Carbonic oxide.

V. Action of the Haloid Elements on Organic Bodies.

(1.) *Chlorine :*—

(α.) It may combine with the organic body, forming an *additive* compound. This happens in the case of certain non-saturated compounds. *Example :*—Benzene (C_6H_6) becomes benzene hexachloride ($C_6H_6Cl_6$).

(β.) It may in the presence of water, oxidize the organic body.

Example : — Benzoic aldehyde (C_7H_6O) becomes benzoic acid ($C_7H_6O_2$).

(γ.) It may effect the removal of hydrogen (as HCl) from the organic body with the substitution of chlorine, forming a *substitution* product. This substitution may be complete or partial, depending upon the substance acted upon, the temperature, etc. Thus we have :—

$C_2H_4O_2$	Acetic acid
$C_2H_3ClO_2$ ...	Chloracetic acid
$C_2HCl_3O_2$ ...	Trichloracetic acid

CH_4	Methane
CH_3Cl	Chlor-methane
CH_2Cl_2 ...	Dichlor-methane
$CHCl_3$	Trichlor-methane
CCl_4	Tetrachlor-methane

(δ.) It may effect the removal of hydrogen (as HCl) from the organic body, but without substitution of chlorine for it. *Example :*—By acting with chlorine on alcohol (C_2H_6O), we form aldehyde (C_2H_4O) ($C_2H_6O + Cl_2 = C_2H_4O + 2HCl$).

(2.) *Bromine.*—The action of bromine is in all respects similar to, but less intense than, that of chlorine.

(3.) *Iodine.*—Like chlorine and bromine, but less actively than either, iodine forms (1) additive compounds (such as $C_2H_4I_2$) with non-saturated bodies, and (2) also acts as an oxidizing agent. Unlike chlorine and bromine, however, it does not form substitution products by direct combination, unless (1) the hydriodic acid formed be immediately decomposed by some such means as by the addition of mercuric oxide to the mixture, whereby HgI_2 is formed ($HgO + 2HI = HgI_2 + H_2O$), or of iodic acid, when free iodine is produced ($HIO_3 + 5HI = 3I_2 + 3H_2O$); or (2) by the decomposition of other chlorine and bromine compounds with potassium iodide. *For example :*—Iodacetic acid ($C_2H_3IO_2$) may be formed from bromacetic acid ($C_2H_3BrO_2$) by the action of potassium iodide. The intense action of hydriodic acid on iodo-derivatives, explains the difficulty of forming substitution compounds by the direct action of iodine.

VI. Action of Nascent Oxygen on Organic Bodies.

The nascent oxygen for this purpose is commonly liberated by the action of dilute sulphuric acid on potassium dichromate.

1. The oxygen may combine with the organic body. *Example :*— Aldehyde (C_2H_4O) becomes acetic acid ($C_2H_4O_2$).

2. It may decompose the organic body, forming two or more oxidized compounds.

3. It may simply remove hydrogen from the organic body. *Example :*—Alcohol (C_2H_6O) becomes aldehyde (C_2H_4O).

4. It may remove hydrogen from the organic body, the oxygen replacing it in equivalent quantity. *Example :*—Alcohol (C_2H_6O) becomes acetic acid ($C_2H_4O_2$).

5. It may remove hydrogen, the oxygen replacing it by twice

its equivalent quantity. *Example*:—Naphthalene ($C_{10}H_8$) becomes naphtho-quinone ($C_{10}H_6O_2$).

6. If the oxidation be intense, then (as in combustion) the carbon and hydrogen of the organic body may be converted into water and carbonic anhydride, the sulphur oxidized, the nitrogen and the haloid elements being set free.

The changes thus effected by the oxidation of organic bodies, are remarkable, and of great interest. By the action of nascent oxygen on salicine (viz., by distilling it with dilute sulphuric acid and potassic bichromate) we obtain the artificial oil of the spiræa, or meadow-sweet. Uric acid ($C_5H_4N_4O_3$) by oxidation becomes alloxan ($C_4H_2N_2O_4$), alloxan by oxidation becoming urea (CH_4N_2O). By the action of nascent oxygen on amylic alcohol (fusel oil) ($C_5H_{12}O$) we form valerianic acid ($C_5H_{10}O_2$), etc.

VII. Action of Nascent Hydrogen on Organic Bodies.

Free hydrogen has no action on organic bodies, but nascent hydrogen acts in many cases powerfully. Nascent hydrogen may be set free either by (1) the action of water on sodium amalgam, or (2) by the action of dilute sulphuric acid on zinc or of hydrochloric acid on tin.

1. The hydrogen may combine with the organic body. *Example*:—Ethene oxide (C_2H_4O) forms alcohol (C_2H_6O).

2. The hydrogen (2 atoms) may remove oxygen (1 atom) from the organic body. *Example*:—Benzoic acid ($C_7H_6O_2$) + H_2 becomes benzoic aldehyde (C_7H_6O) + H_2O.

3. The hydrogen may effect the removal of the haloid elements.

4. The hydrogen may remove oxygen and the haloid elements, and be substituted for them in the compound (*inverse substitution*). The hydrogen may be substituted either (α) in equivalent quantities, or (β) one-half the equivalent of oxygen removed. Thus—

$$(\alpha.)\quad \underset{\text{Benzoic acid}}{C_7H_5O,HO} + 2H_2 = H_2O + \underset{\text{Benzylic alcohol.}}{C_7H_7,HO.}$$

$$(\beta.)\quad \underset{\text{Nitrobenzene}}{C_6H_5(NO_2)} + 3H_2 = 2H_2O + \underset{\text{Aniline.}}{C_6H_5(NH_2).}$$

VIII. Action of Other Reagents on Organic Bodies.

1. Zinc chloride, hydric-potassium sulphate, sulphuric and phosphoric oxides, act as dehydrating agents.

2. Phosphoric chloride (PCl_5) either (α) removes hydrogen from the organic body, an equivalent of chlorine being substituted for it; or (β), removes oxygen from a compound, replacing it by its equivalent of chlorine; or (γ), removes hydroxyl, one of the group HO being replaced by one of chlorine.

3. Sulphurous acid is a powerful reducing agent. In the presence

of a third body having a tendency to combine with hydrogen, it decomposes water and forms sulphuric acid by combining with the oxygen, hydrogen being set free.

4. Chromic acid. This acid acts as a powerful oxidizing agent on organic bodies.

IX. The Action of Light and Electricity on Organic Bodies.

(1.) *The Action of Light.*—The combinations of chlorine with many organic bodies, is as much influenced by light, as the combination of chlorine and hydrogen. Thus chlorine and benzene combine immediately in bright sunlight, slowly in diffused light, but not at all in the dark. The decomposition of hydrocyanic acid is greatly accelerated by light : hence the acid is preserved in blue bottles. Moreover, in some cases the compound formed differs according to the intensity of the light ; thus a mixture of chlorine and mono-chlor-propylene (C_3H_5Cl) forms di-chlor-propylene ($C_3H_4Cl_2$) in the dark, but the compound ($C_3H_5Cl_3$) in bright sunlight.

A well-known action of light is its power of forming the green chlorophyll of leaves ; but we note also a special action of sunlight in elaborating organic compounds generally, in the organisms of growing plants.

(2.) *The Action of the Galvanic Current.*—The organic body is often decomposed, oxygen being formed at the positive pole, and hydrogen at the negative (from the decomposition of the water), these bodies acting powerfully in their nascent condition on the organic compound.

Professor J. H. Gladstone and Mr. Tribe have published a series of researches on the action of the copper-zinc couple ; that is, a very intimate mixture of powdered copper and zinc. By means of the galvanic power generated by the action of this mixed metallic powder, the preparation and the decomposition of many organic compounds have been effected. *For example* — the preparation of zinc ethyl ($Zn(C_2H_5)_2$), ethyl hydride ($C_2H_5.H$), diamyl, zinc amyl ($Zn(C_5H_{11})_2$), amyl hydride ($C_5H_{11}.H$), methyl hydride ($CH_3.H$), acetylene (C_2H_2), propylene (C_3H_6), propyl hydride ($C_3H_7.H$); also the discovery of zinc propyl ($Zn(C_3H_7)_2$), zinc isopropyl, zinc propiodide ($ZnC_3H_7.I$), and the ethylo-haloid compounds (as ZnC_2H_5Br); also the isolation of diallyl, the conversion of nitrates into ammonia (Thorpe), etc., etc.

CHAPTER XXI.

CYANOGEN AND ITS COMPOUNDS.

Cyanogen—Hydrocyanic Acid—Cyanides—Compounds of Cyanogen with the Haloids and with Hydroxyl—Sulphocyanic Acid—Double Cyanogen Salts—The Nitroprussides—Prussian Blue—Reactions of Cyanogen Compounds.

CYANOGEN.

CN or Cy. *Molecular weight*, 52. *Molecular volume*, ☐☐. *Specific gravity*, 1·801. *Fuses at* —29·2° F. (— 34° C). *Boils at* —5·3° F. (—20·7° C.).

Derivation.—(*κύανος*, blue ; *γεννάω*, I produce.)

History.—Discovered by Gay Lussac (1815).

Natural History.—Cyanogen is not found in nature in a free state. It is met with in the gases issuing from blast furnaces, and is produced in small quantities during the distillation of pit coal.

Preparation.—(1.) By the action of heat on the cyanides of mercury, silver, or gold ($Hg(CN)_2 = Hg + (CN)_2$). [A brown amorphous, insoluble, non-volatile substance (*paracyanogen* $(CN)_n$) is formed simultaneously with the cyanogen. At a heat of 1548° F. (860° C.), in an atmosphere which does not act upon it, paracyanogen is converted solely into gaseous cyanogen, without leaving any residue, thus proving it to be an isomer of cyanogen.]

(2.) By the dry distillation of ammonium oxalate [$(NH_4)_2 C_2O_4$] or of oxamide [$C_2O_2(NH_2)_2$] :—

$$\underset{\text{Ammonic oxalate}}{(NH_4)_2C_2O_4} = \underset{\text{Water}}{4H_2O} + \underset{\text{Cyanogen.}}{(CN)_2.}$$

Properties.—(*a.*) *Physical.* A colorless gas, having the odor of bitter almonds. It is intensely poisonous. Its specific gravity is 1·801, and its relative weight 26 ; 100 cubic inches weigh 55·714 grs., and 1 litre, 2·3296 grms. A pressure of four atmospheres at 45° F. (7·2° C.) or a cold of —22° F. (—30° C.) condenses it to a colorless liquid, having a specific gravity of 0·87°, and freezing at —29·2° F. (—34° C.) It withstands a very high temperature without decomposition. It is soluble in water (4 vols. in 1 of water) and in alcohol.

(*β.*) *Chemical.* Cyanogen burns in air with a rose-red flame, generating CO_2 and N. Exploded with oxygen (1 vol. of Cy and 2 vols of O) it yields N (1 vol.) and CO_2 (2 vols.). Its solutions (whether aqueous or alcoholic) decompose rapidly, the *primary* products being ammonium oxalate [$(NH_4)_2 C_2O_4$], a brown insoluble matter (azulmic acid), with traces of hydrocyanic (HCN) and cyanic acids ($HCNO$). As *secondary* products, formed by the action of the cyanic acid on the water, we obtain urea $CO(NH_2)_2$ and hydric ammonium carbonate (NH_4HCO_3). The decomposition of the aqueous solution is much retarded by the presence of a mineral acid. Cyanogen was the first well-recognised "compound organic radical." Chemically, it behaves exactly like a monad non-metallic element, or simple acid radical, such as chlorine, etc. Just as chlorine $(Cl)'$ is univalent, the molecule being represented by Cl_2, so cyanogen $(CN)'$ is univalent, its molecule being represented by $(CN)_2$. As chlorine combines with metals to form chlorides (as $AgCl$; $Hg''Cl_2$), so cyanogen combines with metals to form cyanides ($Ag(CN)$; $Hg''(CN)_2$). As chlorine replaces monad elements, so cyanogen replaces monad elements. Cyanogen combines with hydrogen to form hydrocyanic acid (HCN), as chlorine forms hydrochloric acid (HCl).

The reactions of cyanogen with potassic hydrate, again, are exactly analogous to those of chlorine. Thus :—

(*a.*)	$2KHO$	+	Cl_2	=	KCl	+	$KClO$	+	H_2O.
	Potassic hydrate	+	Chlorine	=	Potassic chloride	+	Potassic hypochlorite	+	Water.
(*β.*)	$2KHO$	+	$(CN)_2$	=	$K(CN)$	+	$K(CN)O$	+	H_2O.
	Potassic hydrate	+	Cyanogen	=	Potassic cyanide	+	Potassic cyanate	+	Water.

Thus cyanogen supplies us with a typical illustration of "a compound radical,"—that is, a group of elements, capable of acting exactly as though it were an element. To express this quasi-elementary character of cyanogen, we represent it by the symbol Cy.

Hydrocyanic Acid (Prussic Acid) (HCN or HCy).

Molecular weight, 27. *Molecular volume,* ☐☐. *Specific gravity of liquid at* 44·9° F. (7·2° C.), 0·7058. *Fuses at* 5° F. (—15° C.). *Boils at* 79·7° F. (26·5° C.). *Vapor density,* 0·948.

History.—Discovered by Scheele (1782), who named it *prussic acid.* Its composition was proved by Berthollet (1787).

Natural History.—It is found in cherry-laurel water (*aqua lavrocerasi*), in bitter-almond water, and in water distilled in contact with various plants belonging to the natural order *Rosaceæ*, and with the kernels of many stone fruits. Its formation in these is no doubt due to the ferment action of emulsin or synaptase on amygdalin or some body of a similar nature (*see* page 581).

Preparation.—(1.) By passing electric sparks through a mixture of nitrogen and acetylene :—

N_2	+	C_2H_2	=	$2HCN$.
Nitrogen	+	Acetylene	=	Hydrocyanic acid.

(2.) *Process of B.P. in preparing "acidum hydrocyanicum dilutum."* By distilling potassium ferrocyanide with dilute sulphuric acid:—

$$2K_4FeCy_6 + 3H_2SO_4 = 6HCN + K_2Fe_2Cy_6 + 3K_2SO_4.$$

Potassic ferrocyanide + Sulphuric acid = Hydrocyanic acid + Ferrocyanide of iron and potassium + Potassic sulphate.

The B.P. solution is made to have a specific gravity of 0·997, and to contain 2 per cent. of anhydrous acid; in other words, 100 grains of the dilute acid should yield 10 grains of AgCy when heated with argentic nitrate.

(3.) By the action of acids on metallic cyanides ($KCN + HCl = HCN + KCl$).

Preparation of Scheele's Acid.—Prussian blue and mercuric oxide (HgO) are boiled in water, whereby Fe_2O_3 is precipitated, and a solution of mercuric cyanide ($HgCy_2$) formed. The clear filtrate is then mixed with dilute sulphuric acid, and shaken up with iron filings ($HgCy_2 + Fe + H_2SO_4 = 2HCy + FeSO_4 + Hg$). The solution contains 4 or 5 per cent. of anhydrous acid.

(4.) By heating chloroform with ammonia. (The process is facilitated by the addition of an alcoholic solution of potassic hydrate):—

$$CH.Cl_3 + NH_3 = HCN + 3HCl.$$

Chloroform + Ammonia = Hydrocyanic acid + Hydrochloric acid.

(5.) *Preparation of Anhydrous Acid.*—By decomposing argentic cyanide (gently heated) with sulphuretted hydrogen, or with gaseous hydrochloric acid:—

$$2AgCN + H_2S = Ag_2S + 2HCN.$$

Argentic cyanide + Sulphuretted hydrogen = Argentic sulphide + Hydrocyanic acid.

Properties.—(α.) *Physical.* A colorless, highly volatile liquid, having a bitter almond odor and a bitter taste. It freezes at 0° F. (—19·8° C.), and boils at 79° F. (26·1° C.), emitting a combustible vapor. It is so volatile that during its spontaneous evaporation it freezes the rest of the acid. It mixes with water and alcohol in all proportions. Its physiological action is intense, destroying life rapidly. It is given in medicine, and, largely diluted with air, the vapor is occasionally used as an inhalation (vapor acidi hydrocyanici (B.P.)).

(β.) *Chemical.* Its acid properties are so feeble that it cannot even displace carbonic acid from its compounds. Both the pure acid and its aqueous solution decompose spontaneously (particularly when exposed to the light), various brown substances being deposited, and ammonic oxalate and formate produced. A trace of mineral acid, such as is certain to be present in the B.P. acid, retards the decomposition. [It is worthy of note that when ammonic formate is heated, it yields hydrocyanic acid and water (NH_4CHO_2

$=CNH+2H_2O$).] It forms with the haloid acids additive crystalline bodies, such as ($HCN.HCl$), etc., which are easily decomposed into formic acid and ammonium salts ($HCN.HCl+2H_2O=CH_2O_2$ (formic acid) $+NH_4Cl$). It forms metallic cyanides with metallic oxides and hydrates, but when boiled with an excess of potash it evolves ammonia.

The Cyanides, Chlorides, and Hydroxides of Cyanogen.

The following constitute the most important of these compounds:—

I. Cyanides.

NAME.	Formulæ.	Molecular Weight.	Specific Gravity.	Appearance.	
Potassic cyanide	KCy	65		White cubes	Deliquescent salts, soluble in water and spirit and fusible. Not changed by heat when air is excluded, but in the presence of air, become cyanates. Their solutions, when boiled, yield formates. Solutions alkaline.
Sodic cyanide	$NaCy$	49		do.	
Ammonic cyanide ..	NH_4Cy	44		do.	Very soluble in water; the solution easily decomposes.
Mercuric cyanide . ..	$HgCy_2$	252	3·77	do.	Soluble in water and in alcohol; solution not precipitated by alkalies.
Argentic cyanide	$AgCy$	134	3·94	do.	Insoluble in water.
Zinc cyanide	$ZnCy_2$	91		do.	Do.
Cobaltous cyanide ..	$CoCy_2$	111		do.	Do.
Palladium cyanide ..	$PdCy_2$	158		Yellowish white	Do.
Auric cyanide	$AuCy_3$	275		do.	Insoluble in water; soluble in a solution of KCy.
Ferrous cyanide	$FeCy_2$	108		Yellowish red	Soluble in solution of KCy, forming ($K_4Cy_4Fe''Cy_2$).
Ferric cyanide	Fe_2Cy_6				Only known in solution.

II. Chlorides, etc.

Cyanogen chloride (gaseous)	$CyCl$.
,, ,, (solid)	Cy_3Cl_3.
Cyanogen bromide	$CyBr$.
,, ,, ...	Cy_3Br_3.
Cyanogen iodide	CyI.
Cyanogen sulphide	Cy_2S.

III. Hydroxides, etc.

Cyanic acid	$HCyO$	Potassic cyanate	$KCyO$.
		Ammonic cyanate	NH_4CyO.
		Urea	CH_4N_2O.

Cyanuric acid	$H_3Cy_3O_3$	Argentic cyanurate..	$Ag_3Cy_3O_3$.
		Argentic hydric cyanurate ..	$Ag_2HCy_3O_3$.
		Potassic hydric cyanurate ..	$KH_2Cy_3O_3$
Fulminuric acid ..	$H_3Cy_3O_3$	Potassic hydric fulminurate ..	$K_2HCy_3O_3$.
Cyamelide..	$H_nCy_nO_n$		
Fulminic acid	$Cy_2H_2O_2$	Mercuric fulminate..	$Hg''Cy_2O_2$.
		Argentic fulminate	$Ag_2Cy_2O_2$.
		Ammonic argentic fulminate..	$NH_4AgCy_2O_2$.
Sulphocyanogen ..	CNS or CyS or SCy	Ammonic sulphocyanate.. ..	NH_4CyS.
		Potassic sulphocyanate	KCyS.
Sulphocyanic acid ..	HCyS	Plumbic sulphocyanate	$Pb(CyS)_2$.
		Mercuric sulphocyanate.. ..	$Hg(CyS)_2$.

The Cyanides.

The cyanides are closely allied to the haloid salts.

Preparation of the Metallic Cyanides.

1. By burning the metal either in cyanogen gas, or in the vapor of hydrocyanic acid (KCy; NaCy).

[Ammonic cyanide may be formed by mixing together the vapors of ammonia and of hydrocyanic acid.]

2. By acting on metallic oxides or hydrates with hydrocyanic acid:—

$$(\alpha.)\ HgO + 2HCy = Hg''Cy_2 + H_2O$$

$$(\beta.)\ KHO + HCy = KCy + H_2O.$$

3. By passing nitrogen over a red-hot mixture of a metallic carbonate and carbon:—

$$\begin{array}{ccccccccc} K_2CO_3 & + & 4C & + & 2N & = & 2KCN & + & 3CO. \\ \text{Potassic carbonate} & + & \text{Carbon} & + & \text{Nitrogen} & = & \text{Potassic cyanide} & + & \text{Carbonic oxide.} \end{array}$$

[Thus cyanogen is formed in blast furnaces, the potassic carbonate being supplied by the ash, and the C and N by the fuel.] Ammonic cyanide may be formed by passing ammonia gas over red-hot charcoal.

4. In the case of potassic cyanide it may be prepared either—

(*α*.) By merely heating potassic ferrocyanide—

$$\begin{array}{ccccccc} K_4Fe''Cy_6 & = & 4KCy & + & FeC_2 & + & N_2. \\ \text{Potassic ferrocyanide} & = & \text{Potassic cyanide} & + & \text{Carbide of iron} & + & \text{Nitrogen.} \end{array}$$

(*β*.) Or, by heating a mixture of potassic ferrocyanide and potassic carbonate:—

$$\begin{array}{ccccccccccc} K_4Fe''Cy_6 & + & K_2CO_3 & = & 5KCy & + & KCyO & + & Fe & + & CO_2. \\ \text{Potassic ferrocyanide} & + & \text{Potassic carbonate} & = & \text{Potassic cyanide} & + & \text{Potassic cyanate} & + & \text{Iron} & + & \text{Carbonic anhydride} \end{array}$$

[Prepared in this way commercial potassic cyanide usually contains both potassic cyanate and potassic carbonate.]

If mercuric sulphate be added to the potassic ferrocyanide, mercuric cyanide is formed.

5. By the action of a soluble cyanide, or of hydrocyanic acid, on metallic salts.

(α.) Thus *potassic cyanide* with ammonic chloride, forms ammonic cyanide; with mercuric oxide, mercuric cyanide; with palladium chloride, palladium cyanide, etc.

(β.) Thus *hydro-cyanic acid* with zinc acetate, forms zinc cyanide, etc.

Properties of the Cyanides.—They are all more or less of a white color, and have a bitter-almond odor. In the case of potassic cyanide, it evolves an odor of almonds (from the free hydrocyanic acid present) and ammonia (from the decomposition of the cyanate by moisture):—

$$2KCyO + 4H_2O = K_2CO_3 + (NH_4)_2CO_3.$$

Potassic cyanate + Water = Potassic carbonate + Ammonic carbonate.

All the cyanides are poisonous bodies.

The alkaline cyanides, when fused in the presence of air, become cyanates. Acids decompose certain cyanides readily (*e. g.* potassic cyanide which is even decomposed by carbonic acid), whilst on other cyanides, as aurous cyanide, acids act with difficulty. Most cyanides are soluble in solutions of the alkaline cyanides, forming double cyanides. So rapid is this combination in some cases (*e.g.* with ferrous and ferric cyanides), that the simple cyanides can scarcely be said to exist in a separate state.

Uses.—Potassic cyanide is the most important of the cyanides. It is used (*a*) in *electroplating and gilding*, from its property of dissolving argentic cyanide, forming with it a compound which is easily decomposed with the battery; (β) *in photography*, from its property of dissolving silver, either as a chloride, bromide, iodide, or as the metal; and (γ) *in the laboratory*, as a reducing agent, from its property of abstracting oxygen from bodies at a high temperature to form a cyanate ($SnO_2 + 2KCy = Sn + 2KCyO$).

Cyanogen Chlorides, etc.

Two isomeric chlorides of cyanogen have been described. They are the products of the action of chlorine on hydrocyanic acid, or on a metallic cyanide:—

Gaseous Cyanogen Chloride ($CyCl = 61{\cdot}5$. Mol. vol. ☐☐) is a colorless pungent gas, capable of being liquefied by a pressure of four atmospheres. It is soluble in water, alcohol, and ether. On passing CyCl into a solution of ammonia in anhydrous ether, *cyanamide*, CN_2H_2, and ammonium chloride are formed.

Solid Cyanogen Chloride ($Cy_3Cl_3 = 184{\cdot}5$; Mol. vol. ☐☐) is a crystalline colorless solid. It is soluble in alcohol and ether. It melts at 284° F. (140° C.), and at a higher temperature sublimes unchanged.

This body yields, by distillation, *cyanic acid* ($HCyO$), and by the action of water, *cyanuric acid* ($H_3Cy_3O_3$), a polymer of cyanic acid.

The **Cyanogen Bromides** ($CyBr$ and Cy_3Br_3), and a solid crystalline **Cyanogen Iodide** (CyI), have been prepared. By the action of the latter on sulpho- (or thio-) cyanate of silver, a **Cyanogen Sulphide** (Cy_2S) may be formed.

COMPOUNDS OF CYANOGEN AND HYDROXYL.

Cyanic acid	$CyOH$.
Fulminic acid	$Cy_2O_2H_2$
Cyanuric acid	$Cy_3O_3H_3$.
Fulminuric acid	$Cy_3O_3H_3$.
Cyamelide	$Cy_nO_nH_n$.

Cyanic Acid ($HCyO$ or $CN(OH)=43$) and the Cyanates.

(*a*.) *Preparation of the acid.*—By the distillation of dry cyanuric acid ($Cy_3O_3H_3$) collecting the product in an ice-cold receiver.

(β.) *Preparation of the cyanates* ($M'CNO$).—(1.) By the direct oxidation of the cyanides ($KCy+PbO=Pb+KCNO$).

(2.) By the action of cyanogen gas upon potassic hydrate ($(CN)_2+2KHO=KCN+KCNO+H_2O$). Cyanic acid cannot be prepared by the addition of acids to the cyanates, inasmuch as cyanic acid forms, by combination (α) with *water*, ammonic carbonate, and (β) with *ammonia*, urea, or ammonic cyanate. Thus—

(α.) $Cy(OH)+2H_2O=NH_4HCO_3$ (ammonic carbonate);

(β.) $Cy(OH)+NH_3=CH_4N_2O$ (urea).

Properties.—Cyanic acid is a colorless, pungent, acid liquid. It changes rapidly at 32° F. (0° C.) into cyamelide. It is monobasic.

Ammonium Cyanate (NH_4CyO); *urea* $CO(NH_2)_2$.

Preparation.—(1.) When cyanic acid vapor is mixed with an excess of ammonia, ammonic cyanate is formed. After a short exposure to air, or immediately at 212° F. (100° C.), the salt undergoes a molecular change, and becomes urea. (Wöhler.)

(2.) *Ammonic cyanate* and *urea* may also be prepared by mixing potassic cyanate and ammonic sulphate in water, evaporating the solution to dryness, and dissolving out the urea from the residue with alcohol:—

$$\begin{array}{ccccccccc} 2KCyO & + & (NH_4)_2SO_4 & = & K_2SO_4 & + & 2NH_4CyO. \\ \text{Potassic cyanate} & + & \text{Ammonic sulphate} & = & \text{Potassic sulphate} & + & \text{Ammonic cyanate.} \end{array}$$

Urea is a weak base, and constitutes the chief nitrogenised constituent of urine. It may be obtained as a nitrate [$(CN_2H_4O)HNO_3$] by adding nitric acid to concentrated urine. When an aqueous solution of urea is mixed with oxalic acid, an insoluble oxalate of urea is formed—

$$[(CN_2H_4O)C_2H_2O_4].$$

Urea is decomposed by heat, evolving ammonia, the residue of such ignition constituting cyanuric acid.

In contact with decomposing matter, urea combines with water and becomes ammonic carbonate. Hence the presence of ammonium carbonate in decomposed urine.

$$\underset{\text{Urea}}{CN_2H_4O} \;+\; \underset{\text{Water}}{2H_2O} \;=\; \underset{\text{Ammonic carbonate.}}{(NH_4)_2CO_3.}$$

A compound where the oxygen of the urea has been replaced by sulphur (forming what is called *sulphur-urea* (CN_2H_4S)) has been obtained.

Cyanuric Acid ($Cy_3O_3H_3$ or $C_3N_3(OH)_3$).

Preparation.—(1.) By the action of heat on urea.

(2.) By the action of water on solid cyanogen chloride ($Cy_3Cl_3+3H_2O = 3HCl+Cy_3H_3O_3$). [As water replaces the Cl of cyanogen chloride by the group HO, so phosphorus pentachloride replaces the group HO of cyanuric acid by Cl. ($C_3N_3(OH)_3+3PCl_5=C_3N_3Cl_3+3POCl_3+3HCl$).]

Properties.—Forms colorless efflorescent crystals, which are not soluble in cold water, but are soluble in boiling (1 in 24). The acid is very stable, and is soluble in, but is not decomposed by strong sulphuric or nitric acids. In this respect it contrasts remarkably with its isomer cyanic acid.

Cyanuric acid is a tribasic acid, forming three classes of salts: viz., $M'_3Cy_3O_3$ (as $Ag_3Cy_3O_3$), $M'_2HCy_3O_3$ (as $Ag_2HCy_3O_3$), and $M'H_2Cy_3O_3$ (as $KH_2Cy_3O_3$).

Fulminuric Acid ($H_3Cy_3O_3$ or $C_3N_3(OH)_3$).

Preparation.—By the action of a soluble chloride on mercuric fulminate:—

$$\underbrace{3Hg''Cy_2O_2}_{\text{Mercuric fulminate}}+8KCl+H_2O=4KCl+2HgCl_2+Hg''O+\underbrace{2K_2HCy_3O_3.}_{\text{Potassic fulminurate.}}$$

Fulminuric acid is dibasic, whereas cyanuric acid (with which it is isomeric), is tribasic.

Cyamelide ($Cy_nO_nH_n$, or $Cy_n(HO)_n$.—A white, solid, amorphous body, formed spontaneously from cyanic acid. It is insoluble either in dilute acids, in alcohol, in ether, or in water. By dry distillation it yields cyanic acid.

The relationship of these bodies requires notice:—

1. Cyanic acid may be prepared by heat from cyanuric acid.
2. Ammonic cyanate by the action of heat becomes urea.
3. Urea by heat leaves a residue of cyanuric acid, evolving ammonia.
4. Cyanic acid changes spontaneously to cyamelide.
5. Cyamelide by dry distillation yields cyanic acid.

Fulminic Acid.—This acid has never been isolated. Its probable composition is $H_2Cy_2O_2$. Thus it is polymeric both with cyanic and with cyanuric acids. It is a bibasic acid.

The fulminates are highly explosive bodies. They are formed by dissolving the metal in nitric acid and adding alcohol to the solution.

Fulminate of Mercury ($Hg''Cy_2O_2$) has a specific gravity of 4·4, and is decomposed at a temperature of 360° F. (182·2° C.) or by contact with sulphuric or nitric acid, carbonic oxide, nitrogen, and the free metal being produced ($Hg''Cy_2O_2 = Hg + 2CO + N_2$).

Fulminate of Silver has the composition $Ag_2Cy_2O_2$, and is even more easily decomposed than fulminate of mercury.

Double Fulminates have also been prepared, as, *e.g.*, $NH_4AgCy_2O_2$ and $AgKCy_2O_2$.

Sulphocyanic Acid (HCNS, or HCyS) (*thiocyanic acid*). This is the sulphur analogue of cyanic acid.

Preparation (as an acid solution).—By decomposing lead sulphocyanate suspended in water, with sulphuretted hydrogen.

Properties.—The acid may be obtained as a solid crystalline body from the colorless acid solution prepared as above by cold. It is decomposed by boiling, and also on exposure to air. The acid is is monobasic, and forms salts called sulphocyanates (*thiocyanates*).

Ammonium Sulphocyanate (NH_4CyS) is prepared by neutralizing the acid with ammonia, or by digesting hydrocyanic acid with yellow ammonic sulphide, or by heating a mixture of carbon disulphide and alcoholic ammonia [$CS_2 + 3NH_3 = NH_4HS + NH_4CNS$]. By its distillation at a high temperature a body called *melam* ($C_6H_9N_{11}$) is formed. Melam, by the action of potassic hydrate and heat, forms *mellamine* ($C_3H_6N_6$).

Potassium Sulphocyanate (KCyS) is prepared either (1) by fusing together potassic cyanide and sulphur, or (2) by the fusion of three parts of potassic ferrocyanide with one part of potassic carbonate and two parts of sulphur, in a covered crucible. The mass is then lixiviated, and the salt crystallized from the solution :—

$$K_4Fe''Cy_6 + S_6 = 4KCyS + Fe''(CyS)_2.$$

By the action of chlorine on a solution of potassic sulphocyanate, a yellow insoluble precipitate of *persulphocyanogen* (Cy_3HS_3), is formed. This substance when heated forms a body called *mellone* (C_9N_{13}), an organic radical, which with hydrogen forms an acid called *hydro-mellonic acid* ($H_3C_9N_{13}$). The salts are called *mellonides* (*Examples:* the potassic mellonides $K_3C_9N_{13}$; $K_2HC_9N_{13}$ and $KH_2C_9N_{13}$). The tripotassic mellonide yields insoluble precipitates with salts of silver, mercury, lead, etc., viz., *argentic mellonide* ($Ag_3C_9N_{13}$); *mercuric mellonide* ($Hg_3(C_9N_{13})_2$); *plumbic mellonide* ($Pb_3(C_9N_{13})_2$).

Plumbic Sulphocyanate ($Pb(CyS)_2$) is prepared by acting on potassic sulphocyanate with lead acetate.

Mercuric Sulphocyanate ($Hg''(CyS)_2$) constitutes the toy known as Pharaoh's Serpents.

Ethyl Iso-sulphocyanide(C_2H_5CNS), **propyl iso-sulphocyanide** (C_3H_9CNS), etc., form a class of bodies called *mustard oils.*

These bodies are represented as containing the compound radical *sulphocyanogen* (CyS or Scy).

The *selenio-cyanates* correspond to the sulphocyanates, and have the formula ($M'CNSe$).

Double Salts, etc., of Cyanogen.

	Formulæ.
Ferrocyanogen	$Fe''Cy_6$
Ferrocyanic acid	$H_4Fe''Cy_6$
Potassic ferrocyanide	$K_4Fe''Cy_6$
Cupric ferrocyanide	$Cu''_2Fe''Cy_6$
Plumbic ferrocyanide	$Pb_2Fe''Cy_6$
Ferric ferrocyanide (Prussian blue)	$'Fe'''_4Fe''_3Cy_{18}$
Potassic ferrous ferrocyanide (Everitt's white salt)	$FeK_2Fe''Cy_6$
Potassic nickelous cyanide	$K_2Ni''Cy_4=2KCy,NiCy_2$
Ferricyanogen	$Fe'''Cy_6$
Ferricyanic acid	$H_3Fe'''Cy_6$
Potassic ferricyanide	$K_3Fe'''Cy_6$
Plumbic ferricyanide	$Pb''_3Fe'''_2Cy_{12}$
Ferrous ferricyanide (Turnbull's blue)	$Fe''_3Fe'''_2Cy_{12}$
Potassic ferrous ferricyanide	$Fe''KFe'''Cy_6$
Hydro-nitro-prussic acid	$H_2(NO)Fe''Cy_5$
Sodic nitro-prusside	$Na_2(NO)Fe''Cy_5$

Double Cyanides.

These consist of compounds of an alkaline cyanide or a cyanide of an alkaline earth, with a cyanide of another metal.

Preparation.—By dissolving the cyanide of a heavy metal in an alkaline cyanide.

Properties.—The double cyanides may be divided into two classes:—

(*a.*) The *unstable double cyanides*, which are very poisonous, and are decomposed by a dilute acid (as HCl), hydrocyanic acid being liberated from the alkaline cyanide, either with the precipitation of the metallic cyanide, or with the conversion of both metals into chlorides. Thus:—

$$K_2Ni''Cy_4 \quad + \quad 2HCl \quad = \quad NiCy_2 \quad + \quad 2KCl \qquad 2HCy.$$

Potassic nickelous cyanide + Hydrochloric acid = Nickelous cyanide + Potassic chloride + Hydrocyanic acid.

(β.) The *stable double cyanides*, which are not poisonous. They are not decomposed, like the unstable double cyanides, by a dilute acid, but one of the metals unites with hydrogen to form an acid. Thus :—

$$K_4Fe''Cy_6 + 4HCl = H_4FeCy_6 + 4KCl.$$

Ferrocyanide of potassium + Hydrochloric acid = Hydroferrocyanic acid + Potassic chloride.

The ferrocyanides and ferricyanides are of importance. The pure cyanides of iron, owing to their strong tendency to form double salts have never been prepared.

Ferrocyanogen and **Ferricyanogen.**—These groups, neither of which have been isolated, constitute two compound radicals containing iron, differing from one another only in this, that in ferrocyanogen the iron is *bivalent*, whilst in ferricyanogen it is *trivalent*. Thus :—

Ferrocyanogen.—$Fe''Cy_6$ forms potassic ferrocyanide ($K_4Fe''Cy_6$).

Ferricyanogen.—$Fe'''Cy_6$ „ potassic ferricyanide ($K_3Fe'''Cy_6$, or $K_6'Fe_2^{vi}Cy_{12}$).

It will be further noticed that a ferrocyanide differs only from a ferricyanide by one atom of a monad metal (such as K′) ; hence (*a*) *oxidizing agents* (as Cl and HNO_3) convert ferrocyanides into ferricyanides, whilst (*β*) *reducing agents* (*i. e.*, agents capable of undergoing oxidation or of giving up hydrogen) convert ferricyanides into ferrocyanides. To express the radical ferrocyanogen briefly, the formula (Fcy) is frequently used.

Analogous to ferricyanogen we have compound radicals, where the iron is displaced by other metals, as *cobalticyanogen* ($CoCy_6$), *platinocyanogen* ($PtCy_4$), etc. These bodies are distinguished by forming acids with hydrogen, from which salts (termed *cobalticyanides*, etc.) may be prepared by the displacement of hydrogen (*e.g.*, $K_6Co_2Cy_{12}$;— $K_6Cr_2Cy_{12}$;— $K_6Mn_2Cy_{12}$, etc.).

Ferrocyanic Acid ($H_4Fe''Cy_6$).

Preparation.—(1.) By decomposing plumbic (or cupric) ferrocyanide suspended in water, with sulphuretted hydrogen.

(2.) By decomposing a strong solution of potassic ferrocyanide with hydrochloric acid :—

$$K_4FeCy_6 + 4HCl = H_4Fe''Cy_6 + 4KCl.$$

Potassic ferrocyanide + Hydrochloric acid = Hydroferrocyanic acid + Potassic chloride.

Properties.—A white, crystalline, soluble substance, decomposed by heat into hydrocyanic acid and ferrous cyanide ($H_4FeCy_6 = 4HCy + FeCy_2$), the ferrous cyanide forming Prussian blue by exposure to air ($9FeCy_2 + O_3 = 'Fe'''_4Fe''_3Cy_{18} + Fe_2O_3$). The acid is tetrabasic, and forms salts called *ferrocyanides* ($M'_4Fe''Cy_6$).

Potassium Ferrocyanide.—*Yellow prussiate of potash* ($K_4Fe''Cy_6$, or $4KCy,Fe''Cy_2$, or K_4Fcy, or $K_4Fe(CN)_6$).

Preparation.—(1.) By the action on potassic cyanide, either (*a*) of iron filings, the mixture being freely exposed to the air, or (β) of ferrous hydrate :—

$$(\alpha.)\ 6KCy + Fe + H_2O + O = K_4Fe''Cy_6 + 2KHO.$$

Potassic cyanide + Iron + Water + Oxygen = Potassic ferrocyanide + Potassic hydrate.

$$(\beta.)\ 6KCy + FeH_2O_2 = K_4Fe''Cy_6 + 2KHO.$$

Potassic cyanide + Ferrous hydrate = Potassic ferrocyanide + Potassic hydrate.

(2.) By digesting potassic cyanide, either (α) with ferrous sulphide, or (β) with a soluble ferrous salt :—

$$(\alpha.)\ Fe''S + 6KCy = K_4Fe''Cy_6 + K_2S.$$

Ferrous sulphide + Potassic cyanide = Potassic ferrocyanide + Potassic sulphide.

$$(\beta.)\ FeSO_4 + 6KCy = K_4Fe''Cy_6 + K_2SO_4.$$

Ferrous sulphate + Potassic cyanide = Potassic ferrocyanide + Potassic sulphate.

(3.) In the ordinary process of manufacturing "yellow prussiate," nitrogenised animal matters (such as horns, parings of hides, blood, etc.), are fused in covered iron vessels with crude potassic carbonate and scraps of old iron. Thus—(α.) A *potassic cyanide* is formed—

$$K_2CO_3 + C_4 + N_2 = 2KCN + 3CO;$$

Potassic carbonate + Carbon + Nitrogen = Potassic cyanide + Carbonic oxide;

and also (β) a *ferrous sulphide*, from the combination of the iron with the sulphur, derived partly from the animal matter, and partly from the K_2SO_4 present in the crude potassic carbonate.

The fused mass is now treated with boiling water, when the ferrous sulphide re-acts (as in process 2 (α)) on the potassic cyanide, forming sulphide and ferrocyanide of potassium, the separation of the latter being easily effected by solution and crystallization ($FeS + 6KCy = K_4FeCy_6 + K_2S$). Sometimes, to avoid the formation of potassic sulphide, pure potassic carbonate is used, and the cyanides formed afterwards digested with ferrous carbonate :—

$$FeCO_3 + 6KCy = K_4Fe''Cy_6 + K_2CO_3.$$

Ferrous carbonate + Potassic cyanide = Potassic ferrocyanide + Potassic carbonate.

Properties.—It forms large, tough, yellow crystals ($K_4FeCy_6 + 3H_2O$), which are soluble in both cold and hot water (1 in 4 at 60° F. ; 1 in 2 at 212° F.), and insoluble in alcohol. It is not poisonous.

At a moderate heat the yellow salt becomes white and anhydrous. Heated intensely *in air*, it forms potassic cyanate ; but heated *without air* it forms potassic cyanide, carbide of iron, etc.

With dilute sulphuric acid, it yields hydrocyanic acid, but with strong sulphuric acid, the salt is decomposed ($K_4Fe''Cy_6 + 6H_2SO_4 +$

$6H_2O = 6CO + FeSO_4 + 2K_2SO_4 + 3[(NH_4)_2SO_4]$). By the action of hydrochloric acid, hydroferrocyanic acid (H_4FeCy_6) is precipitated.

Fused with alkaline carbonates, it forms potassic cyanide.

With neutral or acid solutions of many metallic salts, it gives characteristic precipitates. With *ferrous salts*, it forms a light blue potassio-ferrous ferrocyanide ($Fe''K_2Fe''Cy_6$) ; with *ferric salts*, ferric ferrocyanide or Prussian blue ($'Fe'''_4Fe''_3Cy_{18}$) ; with *cupric salts*, a red cupric ferrocyanide ($Cu''_2Fe''Cy_6$) ; with *lead salts*, a plumbic ferrocyanide (Pb_2FeCy_6), etc.

The precipitate with *cobalt*, is yellowish green ; with *uranium*, brown ; and with *zinc*, *cadmium*, *nickel*, *manganese*, *tin*, *lead*, *bismuth*, *antimony*, *silver*, and *mercury*, white. Except the precipitates with zinc and cadmium, they are all insoluble in dilute hydrochloric acid.

Uses.—It is largely used in the manufacture of Prussian blue (*see* p. 618), in the preparation of hydrocyanic acid (*see* p. 606), etc.

Ferricyanic Acid (H_3FeCy_6).

Preparation.—By decomposing plumbic ferricyanide ($Pb_3Fe'''_2Cy_{12}$), suspended in water, with sulphuric acid.

Properties.—A red unstable liquid. By heat, it forms hydrocyanic acid and a hydrated ferric cyanide ($Fe_2Cy_6,3H_2O$).

Potassium Ferricyanide.—*Red prussiate of potash* ($K_3Fe'''Cy_6$, or $3KCy,Fe'''Cy_3$, or $K_6(Fe_2)^{vi}Cy_{12}$).

Preparation.—By the action of an oxidizing agent (such as nitric acid, chlorine, etc.) on potassic ferrocyanide :—

$$\underset{\text{Potassic ferrocyanide}}{2(K_4Fe''Cy_6)} \underset{+}{+} \underset{\text{Chlorine}}{Cl_2} \underset{=}{=} \underset{\text{Potassic ferricyanide}}{2(K_3Fe'''Cy_6)} \underset{+}{+} \underset{\text{Potassic chloride.}}{2KCl.}$$

The chlorine withdraws one-fourth of the potassium from the ferrocyanide. The chlorine must not be used in *excess*, otherwise the salt will be decomposed.

Properties.—A red crystalline salt, permanent in the air, and soluble in water (1 in 4 at 60° F.).

It is decomposed by reducing agents.

Its re-actions are important :—

1. It forms insoluble precipitates of characteristic color with many metallic salts in neutral or in feebly acid solutions ; *e.g.* an *orange* precipitate with zinc or silver ; a *yellow*, with cadmium ; a *green*, with nickel and copper ; a *reddish brown*, with cobalt ; a *brown*, with manganese ; a *white*, with stannous salts, etc.

Excepting those of zinc and tin, the ferricyanides of the above metals are insoluble in dilute hydrochloric acid.

2. (*a*.) *With a ferric* or *persalt of iron* (that is, where the iron is really a hexad, although apparently trivalent, as in $(Fe_2)^{vi}Cl_6$), it gives *no* precipitate, but merely turns the solution a reddish brown color.

(β.) With *a ferrous* or *protosalt of iron* (that is, where the iron is bivalent, as in $Fe''Cl_2$) it gives a deep blue precipitate of *ferrous ferricyanide*, $Fe''_3Fe'''_2Cy_{12}+aq$, which, when dried, constitutes "*Turnbull's blue.*"

[NOTE.—Potassic ferrocyanide forms a blue precipitate (Prussian blue) with ferric salts, but not with ferrous salts, potassic ferricyanide constituting the test for iron as a ferrous salt, in which case a blue precipitate is formed. To distinguish Prussian blue (ferric ferrocyanide, $'Fe'''_4Fe''_3Cy_{18}$) from Turnbull's blue (ferrous ferricyanide, $Fe''_3Fe'''_2Cy_{12}$), add potassic hydrate:—with Prussian blue we obtain potassic ferrocyanide, and *ferric or red oxide of iron* (Fe_2O_3); whilst with Turnbull's blue we obtain potassic ferrocyanide, and *magnetic* or *black oxide of iron* (Fe_3O_4).]

3. The ferricyanide is used in dyeing, a fabric being colored blue when boiled in a solution of the salt acidulated with acetic acid. Mixed with potassic hydrate it forms, as an oxidizing agent, a discharge for indigo. Thus:—

$$2(K_3Fe'''Cy_6) + 2KHO = 2(K_4Fe''Cy_6) + O + H_2O.$$

Potassic ferricyanide + Potassic hydrate = Potassic ferrocyanide + Oxygen + Water.

Nitro-prussides.—*Preparation.*—By the action of nitric acid on the ferro- or ferri-cyanides.

Constitution.—The nitro-prussides may be regarded as containing a radical similar to ferrocyanogen ($Fe''Cy_6$), where one of the monatomic radical (NO) has replaced one of Cy—($Fe''(NO)Cy_5$). This radical is diatomic, inasmuch as Cy_2 of the group remains unsaturated.

Hydro-nitro-prussic acid, $H_2(NO)Fe''Cy_5$, has been prepared in a crystalline form.

Sodium nitro-prusside ($Na_2(NO)Fe''Cy_5+2aq$) is the only salt of importance.

Preparation.—Potassic ferrocyanide is boiled with dilute nitric acid, until a ferrous salt added to the solution gives a slate-colored precipitate. It is then boiled with an excess of sodic carbonate, and the solution filtered and crystallized.

Properties.—A brilliant red crystalline (rhombic) body. The soluble nitro-prussides produce a purple color with a mere trace of an alkaline sulphide.

Ferric Ferrocyanide (Prussian Blue), ($'Fe'''_4Fe''_3Cy_{18}$ or Fe_7Cy_{18} or $3Fe''Cy_2,2'Fe''_2Cy_6$, or $2(Fe_2)^{vi}Cy_6, 3Fe''Cy_2+18H_2O$).

History.—Discovered about 1700. Its true nature was not at first understood. Macquer (1724) discovered that it was decomposed by an alkali, a residue of red oxide of iron resulting. Hence he supposed it must be a compound of oxide of iron with an acid which had a greater affinity for an alkali than for oxide of iron. This view was supported by the fact that when a salt of iron was added to the alkaline solution, the prussian blue was re-formed. Scheele, in 1782, prepared the acid which he called *prussic acid.* Gay-Lussac, in 1815, called prussian blue *prussiate of iron.*

Preparation.—(1.) By the action of potassic ferrocyanide on ferric salts :—

$$3K_4Fe''Cy_6 + 2Fe_2Cl_6 = Fe'''_4Fe''_3Cy_{18} + 12KCl.$$

Potassic ferrocyanide + Ferric chloride = Ferric ferrocyanide + Potassic chloride.

[This precipitate forms what is commercially known as *soluble prussian blue*, the precipitate being soluble in pure water.]

(2.) By the action of a mixture of a ferrous and ferric salt on potassic cyanide. (This constitutes the principle of Scheele's test for HCN.) (*See* page 619.)

$$3Fe''Cl_2 + 2'Fe'''_3Cl_6 + 18KCy = 18KCl + Fe'''_4Fe''_3Cy_{18}.$$

Ferrous chloride + Ferric chloride + Potassic cyanide = Potassic chloride + Prussian blue.

(3.) By the action of oxidizing agents, such as air, nitric acid, chlorine, etc., on the light blue precipitate of potassic ferrous ferro-cyanide (known as *Everitt's white salt* = $FeK_2,FeCy_6$) produced when ferrous salts are precipitated with potassic ferrocyanide :—

$$(\alpha.)\quad K_4Fe''Cy_6 + FeSO_4 = FeK_2,FeCy_6 + K_2SO_4.$$

Potassic ferrocyanide + Ferrous sulphate = Potassic ferrous ferrocyanide + Potassic sulphate.

$$(\beta.)\quad 12(FeK_2,Fe''Cy_6) + 3O_2 = 6(K_4Fe''Cy_6) + 2Fe_2O_3 + 2Fe'''_4Fe''_3Cy_{18}.$$

Potassic ferrous ferrocyanide + Oxygen = Potassic ferrocyanide + Ferric oxide + Prussian blue.

[This process is that ordinarily employed in the manufacture of prussian blue. The prussian blue made in this way, however, is not so pure as that prepared by process 1, the pigment being always more or less mixed with potassic-ferrous-ferricyanide ($Fe''K,Fe''Cy_6$), which has also a blue color, and which, it will be seen, differs only from the potassic-ferrous-ferrocyanide by one potassium atom.]

Properties.—Prussian blue is a hard, blue, and brittle substance, without taste or odor. It is largely used as a pigment, but its color is not of a very permanent nature. That prepared by process 1 is soluble in *pure* water ; that prepared by process 3 is insoluble. Heated in air, it burns freely, leaving a residue of Fe_2O_3. Heated without air, it gives off water, ammonic cyanide and ammonic carbonate, a carbide of iron remaining as a residue.

It is insoluble in *dilute acids,* except in a solution of oxalic acid, this solution forming blue ink. *Strong sulphuric acid* turns it white, the color being restored on dilution with water. It is decomposed by strong nitric and hydrochloric acids. *Alkalies* and *alkaline carbonates* destroy the color, dissolving out a ferrocyanide, and leaving ferric oxide :—

$$'Fe'''_4Fe''_3Cy_{18} + 12KHO = 3K_4Fe''Cy_6 + 2Fe_2O_3 + 6H_2O.$$

Prussian blue + Potassic hydrate = Potassic ferro-cyanide + Ferric oxide + Water.

[Thus the calico printer, in forming a pattern on a fabric dyed with Prussian blue, first discharges the color with an alkali, and then dissolves the ferric oxide formed with a dilute acid.]

(I.) *Tests for Hydrocyanic Acid and the Cyanides:*

(α.) The odor of prussic acid.

(β.) *Argentic Nitrate;* gives with the acid a white precipitate of argentic cyanide (AgCy), insoluble in nitric acid, soluble in alkaline cyanides, *almost* insoluble in ammonia. By these reactions, and also by the precipitate not being readily blackened on exposure, AgCy may be known from AgCl.

The argentic cyanide when heated evolves cyanogen, which burns with a rose-red flame, leaving a residue of reduced silver only.

(γ.) (Scheele's Test.) Add to the acid a few drops of a solution of *potassic hydrate.* Thus a potassic cyanide is formed ($HCN + KHO = KCN + H_2O$). Add to the cyanide solution, a mixture of a *ferrous and ferric salt* (such as ferrous chloride and ferric chloride). The ferrous salt converts the cyanogen into ferro-cyanogen ($FeCy_6$), which combines with the iron of the ferric salt to form prussian blue ($18KCy + 3FeCl_2 + 2Fe_2Cl_6 = 18KCl + Fe_7Cy_{18}$). If to this *dilute sulphuric acid* be added to re-dissolve any excess of the ferrous and ferric hydrates precipitated by the excess of potassic hydrate, pure Prussian blue will be precipitated.

In dilute solutions the reactions are somewhat slow.

[Thus in hydrocyanic acid poisoning, a mixture of solutions of sulphate of iron, perchloride of iron, and potassic hydrate, constitutes the best antidote.]

(δ.) *Mercurous Nitrate;* a grey precipitate of metallic mercury, mercuric cyanide remaining in solution.

(ε.) Place some hydrocyanic acid, or a mixture of a cyanide and hydrochloric acid in a watch-glass. Invert over this a second watch-glass, moistened with a few drops of yellow ammonic sulphide in such manner that the sulphide may be freely exposed to the vapor of the acid. Heat the deposit so formed on the covering glass very gently to dryness. Thus an ammonic sulpho-cyanate (NH_4CNS) is formed :—

$$\underbrace{(NH_4)_2S + S_2}_{} + 2HCy = 2NH_4CyS + H_2S.$$

Yellow ammonic sulphide + Hydrocyanic acid = Ammonic sulpho-cyanate + Sulphuretted hydrogen.

This residue of ammonic sulphocyanate, when touched with a ferric chloride solution, yields the blood-red color of ferric sulphocyanate.

Estimation of Hydrocyanic Acid.—1. Argentic nitrate is added to a known quantity of the solution, and the argentic cyanide formed collected and weighed.

$$\begin{aligned} 100 \text{ grs. of } AgCN &= 19{\cdot}4 \text{ grs. of } CN, \text{ or} \\ &= 48{\cdot}57 \text{ grs. of } KCN. \end{aligned}$$

2. Supersaturate a hydrocyanic acid solution with potash, and add a few drops of a solution of common salt. Add to this a nitrate of silver solution of known strength. Immediately that a permanent precipitate of $AgCl$ occurs, it proves that all the HCN present in the solution has been converted into the soluble double salt $KCyAgCy$, the combination of the chlorine with the silver not occurring until this is complete. (Every 170 of $AgNO_3$ corresponds to 26 of cyanogen, and to 65·1 of KCy.)

(II.) *Tests for the Ferrocyanides:*

Ferric salts; a blue ppt. of Prussian blue ($'Fe'''_4Fe''_3Cy_{18}$). On the addition of an excess of potash the red ferric oxide is produced.

Cupric salts; a red ppt. of cupric ferrocyanide ($Cu''_2Fe''Cy_6$).

(3.) *Tests for the Ferricyanides:*

Ferric salts; no ppt., but merely a reddish-brown solution formed.

Ferrous salts; a blue ppt. of ferrous ferricyanide ($Fe''_3Fe'''_2 Cy_{12}$). On the addition of an excess of potash, the *black* magnetic oxide of iron is produced.

(4.) *Tests for the Sulphocyanates* (Sulphocyanides):

Ferric salts; a blood-red coloration from the formation of ferric sulphocyanate. The red color is discharged on the addition of mercuric chloride.

(5.) *Tests for the Nitro-prussides:*

Alkaline sulphides; a purple color.

CHAPTER XXII.

THE HYDROCARBONS.

Series of Hydrocarbons.—The Paraffins—Chloroform—The Olefines—Acetylene—Turpenes—Benzenes—Naphthalene—Anthracene—Formation of Alizarene.

Supplement.—Paraffin and Petroleum—Turpentine—Volatile Oils—Camphors—Resins—Gum Resins—Oleo-Resins—Balsams—India Rubber—Gutta Percha.

THE HYDROCARBONS.

It will assist us if, before considering the hydrocarbons in detail, we note the following facts:—

1. Carbon is a *tetrad* element. When combined, therefore, with four monad atoms (as in CH_4), it is regarded as fully "saturated."

2. Although, however, the carbon in CH_4 is fully saturated, and is therefore incapable of further combination (in other words, it cannot form *an additive* compound), nevertheless it can exchange one or more unit weights of its hydrogen for an equivalent quantity of some other element (in other words, it can form a *substitution* compound). Thus CH_4 can form CH_3Cl or CH_2Cl_2, etc. These substitution compounds with the halogens are called *haloid derivatives*. Again, it can exchange its hydrogen for a monad group, such as $(CN)'$, $(NO_2)'$, $(NH_2)'$, etc., and thus form other derivatives, as $CH_3(CN)'$, etc.

3. Again, carbon has the property of uniting with itself (*duplication*). Whenever this occurs its atom-fixing power is increased by *at most* two monad units; thus—

1 of carbon can unite with 4 unit weights of hydrogen, etc., to form CH_4
2 of carbon ,, ,, 6 ,, ,, ,, C_2H_6
3 of carbon ,, ,, 8 ,, ,, ,, C_3H_8

This fact has been already represented graphically (*see* page 559).

A series where the members or terms of the series, as they are called, increase by a regular increment of CH_2, is called an *homologous series*. All the members of the series described above are fully saturated.

4. If a saturated hydrocarbon, as CH_4, be deprived of a molecule of hydrogen (H_2), a residual molecule is left (CH_2) which is "non saturated," and gives rise to a new homologous series, all the members of which are also non-saturated molecules; as follows:—

$$CH_2—C_2H_4—C_3H_6—C_4H_8, \text{ etc.}$$

These non-saturated hydrocarbons, however, are able to unite with other elements or compound radicals to form saturated compounds.

5. By an *isologous* series, we imply a series in which the successive terms differ by H_2; thus

Ethane ... ... C_2H_6
Ethene (Ethylene) ... ... C_2H_4
Ethine (Acetylene) ... ... C_2H_2, etc.,

constitute an isologous series.

6. Hydrocarbons of even equivalence (such as those with the formula C_nH_{2n+2}, as CH_4) may exist separately, whilst hydrocarbons of unequal equivalence (as CH_3, *methyl*) are incapable of existing in the free state, unless, perhaps, as double molecules, *i.e.* $\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.=C_2H_6$.

7. A hydrocarbon containing an even number of hydrogen atoms has been regarded as a hydride of a radical containing an uneven number of hydrogen atoms. Thus *methane* (CH_4) may be regarded as a hydride of methyl ($CH_3.H$); *ethane* (C_2H_6) as a hydride of ethyl ($C_2H_5.H$), etc. The groups CH_3, C_2H_5, etc., are called either "hydrocarbon radicals," or, for reasons to be seen directly, "alcohol radicals."

It must, however, be remembered that there is no ground for the belief that one hydrogen of the body CH_4 plays a different part in the compound to the other three.

8. (*α.*) An *alcohol* is a hydrocarbon in which one or more atoms of hydrogen have been replaced by one or more of the group (OH). An alcohol may be regarded as the organic analogue of a metallic hydrate, such as Na (OH). Thus:—

Methane CH_4 forms *methylic alcohol* $CH_3(OH)$, or *methylic hydrate*;
Ethane C_2H_6 „ *ethylic alcohol* $C_2H_5(OH)$, or *ethylic hydrate*; etc.

(*β.*) A *thio-alcohol* or *mercaptan* is, in like manner, the organic analogue of a metallic sulphydrate, as Na(SH); thus

Methylic sulphydrate $CH_3(SH)$; *Ethylic sulphydrate* C_2H_5 (SH), etc.

9. (*α.*) An *oxygen ether* is a compound of hydrocarbon radicals and oxygen. It may, therefore, be regarded as an *alcoholic oxide* or *anhydride.* It will be remarked that the relationship of Na(OH) to Na_2O is an analogous relationship to that existing between an alcohol and an ether. Thus—

Sodic hydrate Na(OH) and *Sodic oxide* Na_2O correspond to
Ethylic alcohol C_2H_5 (OH) and *Ethylic ether* $(C_2H_5)_2O$.

(*β.*) In a sulphur (thio-ether) or selenium ether, which may be regarded as the analogues of metallic sulphides or selenides, the O is replaced by S or by Se; *e.g.*, $(C_2H_5)_2S$, etc.

10. An *aldehyde* is a hydrocarbon where the hydrogen is replaced by the group $(COH)'$. Thus:—

Methane $CH_3.H$ yields *acetic aldehyde* CH_3 (COH).

It may be remarked here that an aldehyde is produced by the oxidation of an alcohol, and an acid by the oxidation of an aldehyde.

Thus an aldehyde stands, as it were, midway between an alcohol and an acid. Thus :—

$$\underset{\text{Ethylic alcohol}}{C_2H_6O} \quad — \quad \underset{\text{Acetic aldehyde}}{C_2H_4O} \quad — \quad \underset{\text{Acetic acid.}}{C_2H_4O_2.}$$

11. A *ketone* is an aldehyde where the H of the group COH in the aldehyde, is replaced by a monad hydrocarbon group. Thus :—

$$\underset{\text{Aldehyde}}{CH_3(COH)} \quad — \quad \underset{\text{Dimethyl ketone.}}{CH_3(CO(CH_3)).}$$

The ketones differ from the aldehydes in the products of their oxidation.

12. An organic *acid* may be regarded as a hydrocarbon where the hydrogen is replaced by the group *carboxyl* (CO.OH)′. Thus :—

$$\underset{\text{Methane}}{CH_4} \; — \; \underset{\text{Acetic acid ;}}{CH_3(COOH) ;} \qquad \underset{\text{Benzene}}{C_6H_6} \; — \; \underset{\text{Benzoic acid.}}{C_6H_5(COOH).}$$

The acids may be regarded, therefore, as oxidized alcohols and aldehydes.

Series of Hydrocarbons.

We have to consider the following series of hydrocarbons :—

Series.	Formula of Series.	Examples.
I. Marsh gas (paraffins)	C_nH_{2n+2}	Methane CH_4 Ethane C_2H_6
II. Olefines	C_nH_{2n}	Ethylene C_2H_4 Propylene C_3H_6
III. Acetylene	C_nH_{2n-2}	Acetylene C_2H_2 Allylene C_3H_4
IV. Turpenes	C_nH_{2n-4}	Quintone C_5H_6 Decone $C_{10}H_{16}$
V. Benzenes (Aromatic series.)	C_nH_{2n-6}	Benzene C_6H_6 Toluene C_7H_8
VI. Cinnamene	C_nH_{2n-8}	Cinnamene C_8H_8 Allylbenzene C_9H_{10}
VII.	C_nH_{2n-10}	Acetenylbenzene C_8H_6
VIII. Naphthalene	C_nH_{2n-12}	Naphthalene $C_{10}H_8$
IX.	C_nH_{2n-14}	Diphenyl $C_{12}H_{10}$
X.	C_nH_{2n-16}	Stilbene $C_{14}H_{12}$
XI. Anthracene	C_nH_{2n-18}	Anthracene $C_{14}H_{10}$
XII.	C_nH_{2n-22}	Diacetenyl-benzene $C_{16}H_{10}$
XIII. Chrysene	C_nH_{2n-24}	Chrysene $C_{18}H_{12}$
XIV.	C_nH_{2n-26}	
XV.	C_nH_{2n-32}	Tetraphenylethylene $C_{26}H_{20}$

Respecting these series we would note generally that—

1. Series II. and III. (viz., the olefine and acetylene series) may be obtained from the Series I. (the paraffins) by similar operations. Further we note that the paraffins do not form additive compounds with the haloids, but that the Series II. and III. (viz., the olefines and acetylene

series) do, being thus rendered compounds of similar constitution to the paraffins. Thus:—

C_2H_2	forms	$C_2H_2Cl_4$	{ a substitution derivative of }	C_2H_6
Acetylene		Tetrachlorethane		Ethane.

2. The paraffins are in all respects a singularly inert class of bodies.

3. Series I., II. and III. do not form nitro-derivatives or sulphonic acids, by their *direct union* with nitric and sulphuric acids.

4. The "terpenes" (Series IV.) are a very stable group. They have a peculiar action on polarized light, and combine readily with the haloids, but they yield neither nitro-derivatives nor sulphonic acids.

5. The benzenes (Series V.), or "*aromatic series,*" as they have been called, and with them Series VIII. and XI., form additive compounds with difficulty, but substitution derivatives with ease, these latter being stable bodies, in some cases not even decomposed by fusion with potassic hydrate. The benzenes form nitro-compounds and sulphonic acids by direct union with nitric and sulphuric acids, by which circumstance they may be distinguished from all the preceding series of hydrocarbons, but not from succeeding series.

6. The naphthalene, anthracene, chrysene and pyrene series of hydrocarbons, form by oxidation "*quinones,*" that is, bodies where two units of hydrogen are replaced by two units of oxygen.

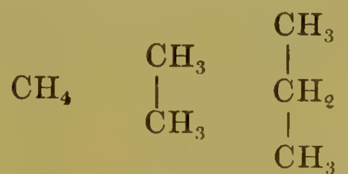
Marsh Gas Series, or Paraffins.

SERIES I.—*Formula* C_nH_{2n+2}.

NAME.	Formulæ.	Boiling point of Normal Paraffin.		Sp. Gr. at deg. Cent.	Remarks.
		F.	C.		
Methane	CH_4				
Ethane	C_2H_6				*Ethyl hydride* $C_2H_5.H$.
Propane	C_3H_8				*Methyl ethyl* $C_2H_5.CH_3$
Butane (*tetrane*)	C_4H_{10}	33·8°	1°	·600 at 0°	*Diethyl* $(C_2H_5)_2$.
Pentane	C_5H_{12}	100·4°	38°	·628 at 17°	
Hexane	C_6H_{14}	158·0°	70°	·669 at 16°	
Heptane	C_7H_{16}	210·2°	99°	·699 at 15°	
Octane	C_8H_{18}	255·2°	124°	·726 at 15°	*Dibutyl* $(C_4H_9)_2$.
Nonane	C_9H_{20}	298·4°	148°	·728 at 13°	
Decane	$C_{10}H_{22}$	334·4°	168°	·739 at 13°	
Undecane	$C_{11}H_{24}$	363·2°	184°	·765 at 16°	
Dodecane	$C_{12}H_{26}$	395·6°	202°	·774 at 17°	
Tridecane	$C_{13}H_{28}$	424·4°	218°	·792 at 20°	
Tetradecane ..	$C_{14}H_{30}$	461·0°	240°	—	
Pentadecane ..	$C_{15}H_{32}$	505·6°	262°	·825 at 16°	
Hexdecane ..	$C_{16}H_{34}$	532·4°	278°		Solid—melts at 69·8° F (21° C.).

The above table represents the gravities and boiling points of the normal primary paraffins. Isomeric modifications of many of these bodies have been prepared, but no isomers are known of the first three terms of the series, viz., methane, ethane, or propane. These isomers are prepared differently, have different gravities and boiling points, and exhibit different reactions. It is customary and convenient to express these varieties by different formulæ, although such expressions must be regarded as merely theoretical, and not in any sense representations of actual molecular construction.

Thus the three first terms of the series have no isomers, and however prepared, exhibit the same chemical and physical properties. Graphically, they may be represented thus :—

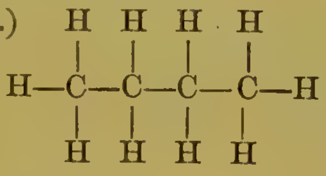


$$CH_4 \qquad \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} \qquad \begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

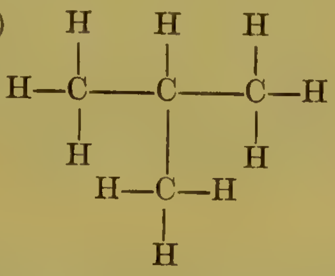
Methane. Ethane. Propane.

This, indeed, is the only way in which it is possible to group the carbon atoms of these bodies. The fourth term C_4H_{10} is derived from the third term by the replacement of one hydrogen atom by the group CH_3. But this displacement of hydrogen may occur in one of two places ; *i.e.*, either in one of the end CH_3 groups, or in the centre CH_2 group. In the one case, none of the carbon atoms would be united with more than *two* carbon atoms, whilst in the second case one of the carbon atoms would be directly combined with *three* carbon atoms. Thus the two forms of the hydrocarbon, butane (C_4H_{10}), may be represented as—

(1.)



or as (2.)



($CH_3.CH_2.CH_2.CH_3$),

Normal butane

No. 1.

($CH_3.CH(CH_3).CH_3$).

Iso-butane.

No. 2.

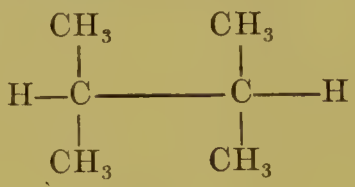
It has been shown that the various isomers (and it is evident that the number of isomers will increase with the advance of a series) may be represented under four heads :—

(1.) *Where each carbon atom is at most associated with two carbon atoms* (No. 1 as figured above). A paraffin so constituted is termed a *normal paraffin.*

(2.) *Where one carbon atom is associated with three carbon atoms*

(No. 2 as figured on the preceding page). A paraffin so constituted is termed an *iso-paraffin.*

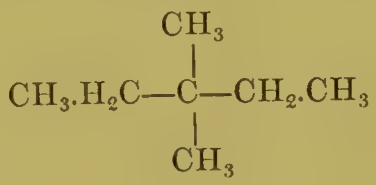
(3.) *Where such group (i.e., one carbon atom being associated with three carbon atoms) occurs twice in a molecule.* A paraffin so constituted has been termed a *meso-paraffin*, as, *e.g.*, in meso-hexane (C_6H_{14}).



$$\begin{array}{ccccc} & \mathrm{CH_3} & & \mathrm{CH_3} & \\ & | & & | & \\ \mathrm{H}- & \mathrm{C} & \text{———} & \mathrm{C} & -\mathrm{H} \\ & | & & | & \\ & \mathrm{CH_3} & & \mathrm{CH_3} & \end{array}$$

No. 3.

(4.) *Where one carbon atom is associated with four other carbon atoms.* A paraffin so constituted has been called by Odling a *neo-paraffin,* as, *e.g.*, in—



$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{CH_3.H_2C-C-CH_2.CH_3} \\ | \\ \mathrm{CH_3} \end{array}$$

No. 4.

Similarly it must be noted that various isomers of the *derivatives* of the paraffins will also result from displacement taking place in different groups. Thus—

$CH_3.CH_2.CH_2I$ = propyliodide (*a–iodopropane*).
$CH_3.CHI.CH_3$ = iso-propyliodide (*β–iodopropane*).

Or again we may have such isomeric compounds as the following:—

$CH_3.CH_2.CH_2.CH_2(OH)$ = Normal butylic alcohol.
$CH(CH_3)_2.CH_2(OH)$ = Iso-primary do.
$C(CH_3)(C_2H_5)H.OH$ = Secondary do.
$C(CH_3)_3(OH)$ = Tertiary do.

Preparation of the Paraffins.—(*General.*) 1. *From the alcohols of the* $C_nH_{2n+1}OH$ *Series.* These are first (a) converted into mono-chlorinated, etc., paraffins by the action of a haloid acid, and afterwards (β) submitted to the action of nascent hydrogen. These actions may be noted in the preparation of ethane;

(a.) $C_2H_5(OH) + HCl = (C_2H_5)Cl + H_2O.$
Ethylic alcohol + Hydrochloric acid = Ethylic chloride + Water.

(β.) $(C_2H_5)Cl + H_2 = C_2H_6 + HCl.$
Ethylic chloride + Hydrogen = Ethane + Hydrochloric acid.

2. By the action on the alcoholic iodides, either (a), of zinc and water, or (β), of zinc alone and heat, in closed vessels :—

(α.) $2C_2H_5I + Zn_2 + 2H_2O = ZnH_2O_2 + ZnI_2 + 2C_2H_6.$
Ethylic iodide + Zinc + Water = Zincic hydrate + Zincic iodide + Ethane.

(β.) $2C_2H_5I + Zn = ZnI_2 + C_4H_{10}.$
Ethylic iodide + Zinc = Zincic iodide + Tetrane.

3. *From the acetic series of acids* by electrolysis :—

$$2C_2H_4O_2 = \overbrace{C_2H_6 + 2CO_2}^{+} + \overbrace{H_2}^{-}.$$

Acetic acid = Ethane + Carbonic anhydride + Hydrogen.

4. *From (α) the acids of the acetic series, and (β) the acids of the succinic series*, by the action of alkalies on their alkaline salts :—

(α.) $KC_2H_3O_2 + KHO = K_2CO_3 + CH_4.$
Potassic acetate + Potassic hydrate = Potassic carbonate = Methane.

(β.) $K_2C_8H_{12}O_4 + 2KHO = 2K_2CO_3 + C_6H_{14}.$
Potassic suberate + Potassic hydrate = Potassic carbonate + Hexane.

General Properties.—(α.) *Physical.* The viscidity of the paraffins increases with their molecular weight, the members of the series becoming gradually less volatile and of higher gravity. Thus the first three terms of the series are gaseous, those next in order are liquid, whilst the final terms are solid.

(β.) *Chemical.* Chlorine, and bromine to a less extent, act directly on the paraffins under the influence of sunlight, to form substitution products, which may be partial or complete. Iodine forms no such compounds directly, but it forms them indirectly. Thus iodine, by its action in the presence of potassic hydrate, on various organic substances, such as sugar, alcohol, etc., forms *iodoform* (CHI_3).

When chlorine acts on the normal primary paraffins, it forms simultaneously two isomeric derivatives, differing in their boiling points and in their specific gravities, and convertible respectively into a normal primary and a normal secondary monohydric alcohol. One or two illustrations will suffice:—

	Boiling point of Derivative.				Specific Gravity, at 0° C.	
	(α.)		(β.)		(α.)	(β.)
	° F.	° C.	° F.	° C.		
CH_3Cl						
C_2H_5Cl	54·5	12·5			0·920	
C_3H_7Cl	115·7	46·5	102·2	39	0·915	0·874 at 10°
C_4H_9Cl	171·5	77·5	158·0	70	0·907	0·895 at 0°
$C_5H_{11}Cl$	223·7	106·5	231·8	111	0·901	0·886 at 0°

With nitric acid paraffins do not form nitro-compounds directly, although nitro-compounds, such as $CH_3(NO_2)$, may be produced by indirect means.

Some of the more important substitution derivatives of the paraffins are stated in the following table :—

Name.	Formulæ.	Preparation and Properties.
Methylic chloride .. (Monochlormethane)	CH_3Cl	*Preparation.*—(1.) By the action of Cl on CH_4 in diffused light. (2.) By the action of HCl gas on methylic alcohol. *Properties.*—A colorless gas, condensing at —4° F. (−20° C.).
Methylene chloride .. (Dichlormethane)	CH_2Cl_2	*Preparation.*—By the action of Cl on CH_3Cl in sunshine. *Properties.*—A colorless liquid; specific gravity, 1·36; boils at 107·6° F. (42° C.)
Chloroform .. .. .. (Trichlormethane)	$CHCl_3$	*Preparation.*—By the action of Cl on CH_4.
Carbonic Tetrachloride . (Tetrachlormethane)	CCl_4	*Preparation.*—(1.) By the action of chlorine on chloroform in sunlight. (2.) By the action of Cl on warm CS_2. *Properties.*—A colorless liquid; specific gravity, 1·6; boils at 172·4° F. (78° C.). By the action of nascent hydrogen CCl_4 may be successively reduced to CH_4.
Iodoform .. .. .. (Tri-iodo-methane)	CHI_3	*Preparation.*—By the action of iodine on alcohol, etc., in the presence of potassic hydrate. *Properties.*—A yellow crystalline body, soluble in alcohol and in ether. It forms cyanoform, $CH(CN)_3$, when heated with mercuric cyanide.
Bromoform	$CHBr_3$	
Nitro-methane	$CH_3(NO_2)$	*Preparation.*—By the action of argentic nitrate on methylic iodide ($CH_3I+AgNO_2 = AgI+CH_3NO_2$). *Properties.*—An oily liquid; boils at 210·2° F. (99° C.) Forms with NaHO the derivative $CH_2Na(NO_2)$.
Nitro-ethane..	$C_2H_5(NO_2)$	*Preparation.*—By the action of argentic nitrate on ethylic iodide. *Properties.*—A colorless liquid; boils at 235·4° F. (113° C.). By the action of nascent hydrogen, forms *ethylamine.*
Cyano-ethane or Ethyl cyanide	$C_2H_5(CN)$	When methyl or ethyl iodide is heated with argentic cyanide, two isomeric ethyl or methyl liquid compounds are formed :— *Ethyl compounds :* (1.) boils at 191·3° F. (88·5° C.); no odor. ,, (2.) boils at 174·2° F. (79° C.); intolerable odor.
Cyano-methane or Methyl cyanide	$CH_3(CN)$	*Methyl compounds :* (1.) boils at 170·6° F. (77° C.); not acted on by acids. ,, (2.) boils at 131° C. (55° C.); decomposed by acids.

Cyano-paraffins.—These compounds may be regarded as paraffin derivatives, either where three atoms of hydrogen have been substituted by trivalent nitrogen, or where one atom of hydrogen has been substituted by the univalent radical Cy. Thus *methyl cyanide* may be regarded either as azo-ethane or as *cyano-methane*, and would be represented accordingly either as $N \equiv C\text{–}CH_3$ or CH_3Cy.

Amido-paraffins.—These compounds may be regarded either (α) as paraffin derivatives where one or more hydrogen atoms in a paraffin are replaced by their equivalent of $(NH_2)'$ (*e.g.*, amido-ethane, or ethylamine $C_2H_5(NH_2)$), or (β) as ammonia derivatives (hence termed *amines*), where one or more hydrogen atoms of the ammonia have been replaced by their equivalents of hydrocarbon radicals (*e. g.*, ethylamine may be regarded as $NH_2(C_2H_5)$).

Nitro-paraffins.—$C_nH_{2n+1}(NO_2)$, are formed by the action of silver nitrite on the iodo-paraffins or alcoholic iodides ($CH_3I + Ag.NO_2 = AgI + CH_3(NO_2)$), and are converted into amido paraffin (*amines*) by the action of nascent hydrogen ($CH_3(NO_2) + 3H_2 = 2H_2O + CH_3(NH_2)$).

Methane (Methylic hydride). *Marsh gas; fire damp* (CH_4), (page 271). [*Molecular weight,* 16. *Specific gravity,* ·557.]

This gas is found arising from decomposing vegetable matter in stagnant pools, also mixed with air in coal mines, where it forms the dangerous mixture fire-damp. It is formed by the destructive distillation of coal, and is the most abundant hydrocarbon in ordinary coal gas. It is most readily prepared by heating a mixture of 2 parts sodic acetate, 2 parts caustic potass, and 3 parts quick lime.

$$NaC_2H_3O_2 + KHO = NaHCO_3 + CH_4.$$

It is a colorless and inodorless gas, and burns with a blue non-luminous flame.

Trichloromethane (Chloroform). *Terchloride of formyle; methenyl chloride; dichlorinated methylic chloride* ($CHCl_3$). [*Molecular weight,* 119·5. *Specific gravity,* 1·525, *at* 0° C. *Boils at* 141·8° F. (61° C.). *Vapor density* (*air*=1) 4·20.]

Preparation.—(1.) By the action of chlorine on methane.

(2.) (*Commercial method.*) By distilling 1 part of alcohol (wood spirit being sometimes employed) with 6 parts of chloride of lime (*bleaching powder*), and 24 parts of water. The distillate consists of water and chloroform, which, on standing, separates into two layers, the water swimming on the chloroform. The exact reaction is doubtful. Probably (α) chloral is formed in the first stage, and (β) in the next stage is decomposed by the calcic hydrate; thus—

(α.) $C_2H_5(OH)$	+	$4Cl_2$	=	$5HCl$	+	CCl_3COH.
Alcohol	+	Chlorine	=	Hydrochloric acid	+	Chloral.
(β.) $2CCl_3COH$	+	CaH_2O_2	=	$Ca''(CHO_2)_2$	+	$2CHCl_3$.
Chloral	+	Calcic hydrate	=	Calcic formate	+	Chloroform.

The chloroform is afterwards purified from certain oils distilling along with it, by agitation with oil of vitriol, on which the chloroform floats. It is drawn off from the acid and again distilled.

(3.) By the action of alkalies on chloral hydrate

$$CCl_3.CH(OH)_2 + NaHO = CHCl_3 + NaHCO_2 + H_2O.$$

Properties.—(*a.*) *Physical.* A colorless liquid, having a fragrant odor and a sweet taste. Specific gravity, 1·48. It is insoluble in water, but miscible with ether and alcohol in all proportions.

(*β.*) *Chemical.* Chloroform burns with difficulty with a greenish flame. Sulphuric acid has no action upon it. Boiled with nitric acid, it forms *chloropicrin* (*nitrotrichlormethane* [$C(NO_2)Cl_3$], a colorless liquid, having a specific gravity of 1·6, and boiling at 233·6° F. (112° C.). Boiled with a solution of potassic hydrate chloroform forms potassic chloride and formate ($CHCl_3 + 4KHO = 3KCl + CHO(OK) + 2H_2O$). When heated with potassium amalgam, *acetylene* (C_2H_2) is set free. Distilled in a current of chlorine, it forms CCl_4. If a solution containing a small quantity of chloroform be heated with aniline and alcoholic soda, a penetrating unpleasant smell of *carbamine* will be observed.

Uses.—As an anæsthetic. For dissolving caoutchouc, and for extracting the alkaloids from organic matters.

(*See* SUPPLEMENTARY CHAPTER.)

The Olefines.

SERIES II.—*Formula* C_nH_{2n}.

The following hydrocarbons of this series have been obtained :—

	Formulæ	Melting point.		Boiling point.		
		° F.	° C.	° F.	° C.	
Ethylene (ethene) ..	C_2H_4					See page 272.
Propylene (propene) ..	C_3H_6			—0·4	—18	
Butylene (quartene) ..	C_4H_8			33·8	1	
Amylene (pentene) ..	C_5H_{10}			95	35	A colorless liquid
Hexylene (sextene) ..	C_6H_{12}			149	65	
Heptylene (septene) ..	C_7H_{14}			204·8	96	
Octylene (octene) ..	C_8H_{16}			248	120	
Nonylene (nonene) ..	C_9H_{18}			284	140	
Diamylene (decene) ..	$C_{10}H_{20}$			320	160	
Triamylene	$C_{15}H_{30}$			482	250	
Cetene (sexdecene) ..	$C_{16}H_{32}$			527	275	
Tetr-amylene	$C_{20}H_{40}$			752	400	
Cerotene	$C_{27}H_{54}$	134·6	57		(?)	
Melissene (melene) ..	$C_{30}H_{60}$	143·6	62	707	375 (?)	

Preparation of the Olefines (*General*).—1. From the *alcohols* of series $C_nH_{2n+1}OH$, by abstracting the elements of water by dehydrating reagents (such as sulphuric acid). Thus :—

$$C_2H_5.OH = C_2H_4 + H_2O.$$

Ethylic alcohol = Ethylene + Water.

2. From the *paraffins*. (*a*.) By the action of lime or potassic hydrate on their mono-haloid derivatives. Thus :—

$$C_4H_9I + KHO = C_4H_8 + KI + H_2O.$$

Iodotetrane + Potassic hydrate = Butylene + Potassic iodide + Water.

(*β*.) By the action of sodium on a mixture of a mon-iodo-paraffin and a mon-iodo-olefine.

(*γ*.) By the decomposition of a mon-iodo-paraffin. At the moment that the monad radical is set free, its transformation, by the action of zinc or sodium, into the dyad radical and the hydride of the monad radical, may be accomplished. This is seen in the formation of ethylene :—

$$2C_2H_5I + Zn = C_2H_4 + ZnI_2 + C_2H_5.H.$$

Ethylic iodide + Zinc = Ethylene + Zincic iodide + Ethylic hydride.

(*δ*.) By the action of a mon-iodo-paraffin on a sodium compound of the same radical. Thus :—

$$C_2H_5I + C_2H_5Na = C_2H_4 + NaI + C_2H_5H.$$

Ethylic iodide + Sodium ethyl = Ethylene + Sodic iodide + Ethylic hydride.

3. From *other simpler hydrocarbons* by direct synthesis. Thus :—

(*a*.) $C_2H_2 + H_2 = C_2H_4.$

Acetylene + Hydrogen = Ethylene.

(*β*.) $2CH_4 + CO = C_3H_6 + H_2O.$

Methane + Carbonic oxide = Propylene + Water.

4. From acids of the $C_nH_{2n}(CO.OH)_2$ series by electrolysis.

Properties (*General*).—(*a*.) *Physical*. The lower members of this series are gaseous ; the higher are solid ; the intermediate terms are liquid.

(*β*.) *Chemical*. The olefines are dyad radicals. Thus they unite with two atoms of the haloids (as $C_2H_4Br_2$), or with one of oxygen (as C_2H_4O). They unite directly with the haloids, to form compounds which are decomposed by an alcoholic solution of potassic hydrate. Thus :—

$$C_2H_4Cl_2 + KHO = KCl + H_2O + C_2H_3Cl.$$

Ethylene dichloride + Potassic hydrate = Potassic chloride + Water + Chlor-ethylene.

The compound C_2H_3Cl may be made to combine with Cl_2 to form the compound $C_2H_3Cl_3$. When this is decomposed with alcoholic potash it forms the compound $C_2H_2Cl_2$. These operations may be repeated until C_2Cl_4 is formed, which body will also combine with Cl_2 to form the solid "per substituted" paraffin, C_2Cl_6.

By the action of alcoholic potash on a monochlorinated (or monobrominated) olefine, a hydrocarbon of the acetylene series C_nH_{2n-2} is formed. Thus :—

$$\begin{array}{ccccccccc} C_2H_3Br & + & KHO & = & KBr & + & H_2O & + & C_2H_2. \\ \text{Bromethylene} & + & \text{Potassic hydrate} & = & \text{Potassic bromide} & + & \text{Water} & + & \text{Acetylene.} \end{array}$$

With *strong sulphuric acid,* certain of the olefines form *ethereal salts,* or, as they are called, acid ethers of sulphuric acid (as $C_2H_4+H_2SO_4 = C_2H_5.HSO_4$). These, when heated with water, are decomposed into sulphuric acid and the monohydric alcohol corresponding to the olefine (thus, $C_2H_5.HSO_4+H_2O=H_2SO_4+C_2H_5(OH)$). With *fuming sulphuric acid* (*i.e.,* an acid containing SO_3 in solution), such olefines form *sulpho-acids* (and not acid ethereal salts), which sulpho-acids are not decomposed by water.

A paraffin may be formed directly from an olefine by the action of nascent hydrogen ; but the change is more easily effected indirectly. Thus by heating ethylene iodide ($C_2H_4I_2$) in closed tubes for some hours with water, *ethane* (C_2H_6) is formed. This conversion is due to the hydrogen, set free by the decomposition of one portion of the ethylene iodide (α), acting on a second and undecomposed portion (β). Thus :—

$$\begin{array}{cccccccccc} (\alpha.) & C_2H_4I_2 & + & 4H_2O & = & 6H_2 & + & 2CO_2 & + & I_2. \\ & \text{Ethylene iodide} & + & \text{Water} & = & \text{Hydrogen} & + & \text{Carbonic anhydride} & + & \text{Iodine.} \end{array}$$

$$\begin{array}{cccccccc} (\beta.) & C_2H_4I_2 & + & H_2 & = & C_2H_6 & + & I_2. \\ & \text{Ethylene iodide} & + & \text{Hydrogen} & = & \text{Ethane} & + & \text{Iodine.} \end{array}$$

The haloid compounds of the olefines, when treated with potassic acetate, form diatomic acetic ether by the exchange of their haloid element for the acid radical—

$$C_2H_4Br_2+2KC_2H_3O_2 = 2KBr+(C_2H_4)(C_2H_3O_2)_2.$$

And these acetic ethers, when distilled with caustic potash, yield diatomic alcohols (*glycols*)—

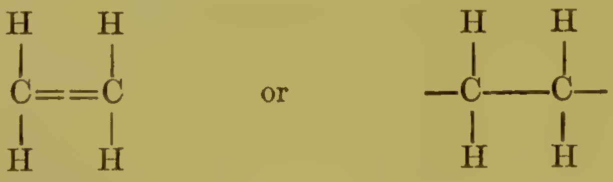
$$(C_2H_4)(C_2H_3O_2)_2+2KHO = 2C_2H_3O_2K+(C_2H_4)(OH)_2.$$

The olefines form monochlorinated monohydric alcohols with hypochlorous acid (α), which, by the action of nascent hydrogen may be converted into the corresponding alcohols (β). Thus—

$$(\alpha.)\ C_2H_4 + ClOH = C_2H_4Cl(OH).$$

$$(\beta.)\ C_2H_4Cl(OH) + H_2 = C_2H_5(OH) + HCl.$$

Lastly, the olefines may exist either as saturated hydrocarbons or as dyad radicals, the difference depending on the linking of the carbon particles. Thus we may represent ethylene, either as



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array} \quad \text{or} \quad \begin{array}{ccccc} & H & & H & \\ & | & & | & \\ - & C & - & C & - \\ & | & & | & \\ & H & & H & \end{array}$$

Saturated or as a dyad radical.

Acetylene Series.

SERIES III.—*Formula* C_nH_{2n-2}.

This includes the following bodies, isomeric modifications of most of the terms of which are known :—

NAME.	Formulæ.	Boiling point.	
		F.	C.
Acetylene (ethine)	C_2H_2		
Allylene (propine)	C_3H_4		
Crotonylene (quartine)	C_4H_6	64·4°	18·0°
Valerylene (quintine)	C_5H_8	113·0°	45·0°
Diallyl (sextine)..	C_6H_{10}	136·4°	58·0°
Rutylene (decine)	$C_{10}H_{18}$	302·0°	150·0°

Preparation of the Acetylene Series (*General*).—1. *From the olefines.*—By acting on a mono-haloid derivative of an olefine, either with alcoholic potash, or with sodic ethylate, at a temperature of 302° F. (150° C.).

(*α*.) $C_2H_3Br + KHO = KBr + H_2O + C_2H_2$.

(*β*.) $C_2H_3Br + C_2H_5NaO = NaBr + C_2H_5(OH) + C_2H_2$.

2. *From the acids of the maleic series* [$C_nH_{2n-2}(COOH)_2$], by electrolysis :—

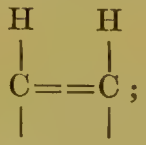
$$\begin{array}{ccccccccc} C_4H_4O_4 & = & C_2H_2 & + & 2CO_2 & + & H_2. \\ \text{Fumaric acid} & = & \text{Acetylene} & + & \text{Carbonic anhydride} & + & \text{Hydrogen.} \end{array}$$

Properties.—(*a*.) *Physical.* Acetylene and allylene are gases. The remaining terms of the series are liquids.

(*β*.) *Chemical.* The acetylene series may either exist in a free state, or act as divalent or quadrivalent radicals; thus—

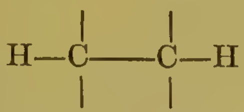
$H—C\equiv C—H$;

Saturated.



$$\overset{H}{\underset{|}{\overset{|}{C}}}=\overset{H}{\underset{|}{\overset{|}{C}}}\ ;$$

Divalent radical.



$$H—\underset{|}{\overset{|}{C}}—\underset{|}{\overset{|}{C}}—H$$

Quadrivalent radical.

Thus C_2H_2 can combine with the haloids to form $C_2H_2Br_2$ or $C_2H_2Br_4$.

When acetylene gas is passed through a solution of cuprous chloride in ammonia, a brown precipitate (a compound of acetylene with cuprous oxide ($C_2H_2.Cu_2O$) is thrown down. When this precipitate is treated with hydrochloric acid, acetylene is given off (page 275).

Turpene Series.

SERIES IV.—*Formula* C_nH_{2n-4}.

A few only of this series have been prepared synthetically.

	Formulæ.	Boiling point.		
		F.	C.	
Quintone (valylene) ..	C_5H_6	140°	60°	Prepared by the action of potassic hydrate on valerylene dibromide ($C_5H_8Br_2$) and rutylene dibromide ($C_{10}H_{18}Br$) respectively.
Polyterpenes	$C_{10}H_{16}$			
Sesquiterpenes	$C_{15}H_{24}$			

(*See* SUPPLEMENTARY CHAPTER.)

The Aromatic Series.—The Benzenes.

SERIES V.—*Formula* C_nH_{2n-6}.

This includes :—

	Name.	Formulæ.	Boiling point.		
			° F.	° C.	
C_6H_6	Benzene	C_6H_6	176·9	80·5	An isomer is known cal *Dipropargyl.*
C_7H_8	Toluene (methylbenzene)	$C_6H_5.CH_3$	230·0	110	
C_8H_{10}	Xylene (ethylbenzene) ..	$C_6H_5(C_2H_5)$	275·0	135	*Xylene* of coal tar oil principally metaxyle By oxidation it yie *metatoluic acid.*
	Paraxylene } Dimethyl-benzenes	$C_6H_4(CH_3)_2$	276·8	136	
	Metaxylene	$C_6H_4(CH_3)_2$	280·4	138	
	Orthoxylene	$C_6H_4(CH_3)_2$	285·8	141	
C_9H_{12}	Propylbenzene	$C_6H_5(C_3H_7)$ (*a.*)	314·6	157	*Cumene* (mesitylene of c tar oil) may be obtair by heating acetone w sulphuric acid :— $3C_3H_6O=C_9H_{12}+3H_2$
	Isopropylbenzene	$C_6H_5(C_3H_7)$ (*β.*)	303·8	151	
	Ethylmethylbenzene ..	$C_6H_4(CH_3)(C_2H_5)$	320·0	160	
	Mesitylene } Trimethyl-benzenes	$C_6H_3(CH_3)_3$	325·4	163	
	Pseudocumene	$C_6H_3(CH_3)_3$	330·8	166	
$C_{10}H_{14}$	Isobutylbenzene	$C_6H_5(C_4H_9)$ (*β.*)	320·0	160	*Cymene* has been obtair synthetically in all forms except modific tion (*a*).
	Propylmethylbenzene ..	$C_6H_4(CH_3)(C_3H_7)$ (*a.*)	354·2	179	
	Isopropylmethylbenzene. .	$C_6H_4(CH_3)(C_3H_7)$ (*β.*)	348·8	176	
	Diethylbenzene	$C_6H_4(C_2H_5)_2$	354·2	179	
	Ethyldimethylbenzene ..	$C_6H_3(C_2H_5)(CH_3)_2$	363·2	184	
	Tetramethylbenzene ..	$C_6H_2(CH_3)_4$	374·0	190	
$C_{11}H_{16}$	Isoamylbenzene	$C_6H_5(C_5H_{11})$ (*β.*)	379·4	193	
	Isopropyldimethylbenzene	$C_6H_3(CH_3)_2(C_3H_7)$ (*β.*)	370·4	188	
	Diethylmethylbenzene ..	$C_6H_3(CH_3)(C_2H_5)_2$	352·4	178	
$C_{12}H_{18}$	Isoamylmethylbenzene ..	$C_6H_4(CH_3)(C_5H_{11})$ (*β.*)	415·4	213	
$C_{13}H_{20}$	Isoamyldimethylbenzene .	$C_6H_3(CH_3)_2(C_5H_{13})$ (*β.*)	451·4	233	

General Preparation of the Benzenes.—(1.) The benzenes may be obtained from coal tar.

(2.) By the action of sodium on a mixture of a moniodated paraffin with a brominated derivative either of benzene, or of an homologous hydrocarbon :—

$$C_nH_{2n+1}I + C_nH_{2n-7}Br + Na_2 = C_nH_{2n-7}.C_nH_{2n+1} + NaI + NaBr.$$

Properties (*General*).—This group, most of the members of which may be obtained from coal tar naphtha, and be *prepared* synthetically, is called *the aromatic group*, on account of the fragrant odor of many of the series. As a class, the benzenes are very stable bodies, and remarkable for the numerous isomers the various terms afford, toluene standing almost alone in the series in possessing no isomeric modifications.

The aromatic series act as *saturated* molecules, forming substitution rather than additive compounds. In this respect they differ from the former groups, excepting the paraffins, that we have considered, the tendency of which were rather to form additive than substitution compounds.

By the action of sulphuric acid the benzenes form sulphonic acids :—

$$C_6H_6 + H_2SO_4 = C_6H_5.HSO_3 + H_2O.$$

The constitution of these hydrocarbons is important. They all contain a group of 6 carbon atoms ; 24 (6 × 4), therefore, is the total combining or atom-fixing power of the 6 atoms. But 18 of this 24 power is occupied by the combination of the carbon atoms with each other, leaving only a power of 6 to be filled up to form a fully saturated molecule. Thus C_6H_6 may be regarded as a fully saturated hydrocarbon. This is shown in Fig. 1 :—

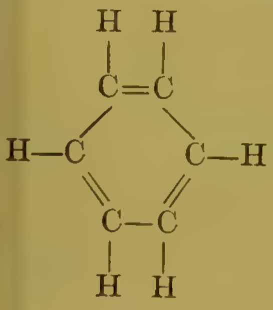


Fig. 1.

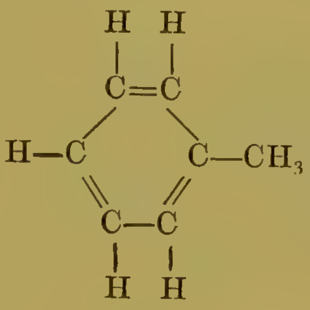


Fig. 2.

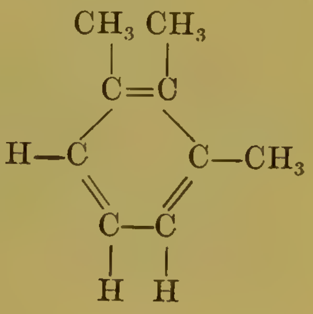
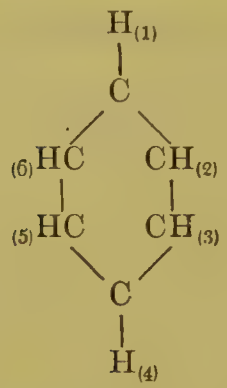


Fig. 3.

It will be seen how other bodies may be derived from this compound by the substitution of more or less complicated molecules in the place of the hydrogen, as in Fig. 2, which represents toluene, or, in Fig. 3, which represents mesitylene (cumene).

The benzene molecule consists of six carbon and six hydrogen atoms. It is usual to represent the structure of benzene as what is called the closed ring in which each carbon atom is directly combined with two carbon atoms and one hydrogen atom, thus :—



This arrangement of the atoms in the benzene molecule shows :—

(1.) The possible formation of additive compounds, *i.e.*, $C_6H_6Br_6$.

(2.) That as all the hydrogens are similarly placed there can be no isomers of the mono-derivatives—only *one* monobromo or mononitro benzene.

(3.) That there are three and only three isomeric di-substitution products, *i. e.*, in which the radical has replaced the hydrogens marked

(α.) 1 and 2,
(β.) 1 and 3,
(γ.) 1 and 4,

because the hydrogens 1 and 2, 2 and 3, 3 and 4, 4 and 5, 5 and 6, and 6 and 1 all bear the same relative positions ; so do 1 and 3, 2 and 4, 3 and 5, 4 and 6, 5 and 1, and 6 and 2, and also 1 and 4, 2 and 5, and 3 and 6 ; thus there are only three possible positions in which the two hydrogens can be replaced.

The di-substitution product, where the radical replaces the hydrogen atoms 1 and 2 (or 1 and 6), is called *ortho;* where 1 and 3 (or 1 and 5) are replaced, it is called *meta*, and where 1 and 4 are replaced, it is called *para*.

The table on page 634 exhibits some of the numerous isomers of this series. We shall note isomeric compounds made up of *the same* groups, as *e.g.*, 3 dimethyl benzenes, $C_6H_4(CH_3)_2$, as well as isomeric compounds made up of *different* groups, such as *ethylbenzene* $(C_6H_5)(C_2H_5)$ and *dimethylbenzene* $(C_6H_4)(CH_3)_2$. The nature of these hydrocarbons is to be specially inferred *by their behaviour on oxidation*, as when treated with dilute nitric or chromic acids. The following facts on this point must be noted :—

(1.) *Benzene* forms no oxidation products that contain 6 carbon atoms. It may be burnt and form H_2O and CO_2. It may also be made to form benzoic acid $(C_7H_6O_2)$ or phthalic acid $(C_8H_6O_4)$.

(2.) All the derivatives of benzene formed by the replacement of one atom of hydrogen by the group C_nH_{2n+1}, such as *methylbenzene*,

$C_6H_5(CH_3)$, *propylbenzene*, $C_6H_5(C_3H_7)$, *butylbenzene*, $C_6H_5(C_4H_9)$, *amylbenzene*, $C_6H_5(C_5H_{11})$, etc., yield, by oxidation, one and the same acid, *viz.*, *benzoic acid*, $C_6H_5(COOH)$.

(3.) The derivatives formed by the replacement of H_2 by two groups of the formula C_nH_{2n+1}, such as *dimethylbenzene*, $C_6H_4(CH_3)_2$, or *diethylbenzene*, $C_6H_4(C_2H_5)_2$, produce by oxidation, in the first instance, an acid of the benzoic acid series, whilst they all finally yield the same acid, *viz.*, *terephthalic acid*, $C_6H_4(COOH)_2$.

(4.) The derivatives formed by the replacement of H_3 by three groups of the formula C_nH_{n+1}, such as *trimethylbenzene*, $C_6H_3(CH_3)_3$, etc., yield on oxidation as their final product *mesitic acid*, $C_6H_3(COOH)_3$.

The molecular constitution of these bodies may be further inferred by their synthetical formation. Thus *methylbenzene* or *toluene* $C_6H_5(CH_3) = (C_7H_8)$ is obtained by the action of sodium on a mixture of *methylic* iodide and bromobenzene ; *ethylbenzene* or *xylene*, $C_6H_5(C_2H_5) = (C_8H_{10})$ is obtained by the action of sodium on a mixture of *ethylic* iodide and bromobenzene ; whilst *dimethylbenzene*, $C_6H_4(CH_3)_2 = (C_8H_{10})$, an isomer of xylene, is formed by the action of sodium on iodomethane and dibromobenzene.

Chlorine and bromine form substitution and additive compounds with benzene *in the presence of iodine.* The iodine acts in such cases as the carrier of chlorine, that is, the chloride of iodine forms moniodobenzene with the benzene, which, by the action of a further portion of iodine chloride, is converted into chlorobenzene. Thus—

(*a.*) $C_6H_6 + ClI = C_6H_5I + HCl.$
Benzene + Iodine chloride = Iodobenzene + Hydrochloric acid.

(β.) $C_6H_5I + ClI = C_6H_5Cl + I_2.$
Iodobenzene + Iodine chloride = Chlorobenzene + Iodine.

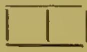
Iodobenzenes may be formed by the action of iodine on benzene *in the presence of iodic acid.* The iodic acid decomposes the hydriodic acid as soon as formed (2). If iodic acid was not added, the hydriodic acid would decompose the iodo derivative, by withdrawing iodine from it and replacing it by hydrogen (1). The following equations will explain this :—

(1.) *Without iodic acid;* $C_6H_5I + HI = C_6H_6 + I_2.$

(2.) *With iodic acid;* $C_6H_5I + 5HI + HIO_3 = C_6H_5I + 3H_2O + 3I_2.$

On toluene in the cold, chlorine forms the stable compound *chlorotoluene* (C_7H_7Cl), which is unaffected, either by nascent hydrogen or by fusion with alkalies. *On boiling toluene*, chlorine forms *benzylic chloride* (C_7H_7Cl), a body having the same composition as chlorotoluene, but differing from it, in that nascent hydrogen changes it to toluene, and alkalies readily decompose it. *On boiling toluene, however, in the presence of iodine*, the stable body *chlorotoluene* is formed, which, as we have said, is singularly unamenable to the action of ordinary reagents.

With strong nitric acid the benzenes form nitro derivatives [$C_6H_6 + HNO_3 = H_2O + C_6H_5(NO_2)$]. With sulphuric acid they form sulphonic acids [$C_6H_6 + H_2SO_4 = H_2O + C_6H_5(HSO_3)$]. With hydriodic acid, aided by a continuous heat of 536° F. (280° C.) they are converted into the corresponding paraffins.

Benzene.—*Benzol; bicarburet of hydrogen; phenylic hydride* (C_6H_6). [*Molecular weight*, 78. *Molecular volume,* . *Boils at* 176·9° F. (80·5° C.).]

Preparation.—(1.) By the action of heat on acetylene ($3C_2H_2 = C_6H_6$).

(2.) By (α) the distillation of benzoic acid with lime, or (β) by the action of heat only on benzoic acid :—

$$(\alpha.)\quad \underset{\text{Benzoic acid}}{C_6H_5(CO.OH)} + \underset{\text{Lime}}{CaH_2O_2} = \underset{\text{Calcic carbonate}}{CaCO_3} + \underset{\text{Water}}{H_2O} + \underset{\text{Benzene.}}{C_6H_6.}$$

$$(\beta.)\quad \underset{\text{Benzoic acid}}{C_6H_5(COOH)} = \underset{\text{Carbonic anhydride}}{CO_2} + \underset{\text{Benzene.}}{C_6H_6.}$$

Its preparation from that portion of the coal tar boiling below 180° F. (82·2° C.) has been already referred to.

Properties.—(a.) *Physical.* A colorless, inflammable liquid of high refracting power, having an ethereal odor and a burning taste. Its Sp. gr. at 0° C. is 0·889. It boils at 176·9° F. (80·5° C.), and solidifies at 41·9° F. (5·5° C.) to a white crystalline solid. It is insoluble in water, but is soluble in alcohol and in ether, and is a solvent for iodine, sulphur, phosphorus, fats, resins, etc. When its vapor is passed through a porcelain tube heated to bright redness, it is decomposed into the gases *hydrogen* and *acetylene* (C_2H_2), into the liquids *diphenyl* ($C_{12}H_{10}$) and *chrysene* ($C_{18}H_{12}$), and into an orange-colored solid called *benzerythrene.* A black liquid, which solidifies on cooling, remains in the retort, and is called *bitumene.*

(β.) *Chemical.* With the haloids, benzene forms both additive and substitution compounds, but the additive compounds are very unstable, breaking up into the substitution products. As illustrations of the *additive compounds* that benzene forms, we have *benzene hexachloride* ($C_6H_6Cl_6$) and *benzene hexabromide* ($C_6H_6Br_6$), both of which are solid bodies, formed by the action of sunlight on a mixture of chlorine and benzene. As illustrations of *substitution compounds,* we have monochlorobenzene, C_6H_5Cl, the compounds $C_6H_4Cl_2$, $C_6H_3Cl_3$, etc.

Some of the benzene derivatives are stated in the following table :—

	Formulæ.	Boiling point.		Melting point.	
		° F.	° C.	° F.	° C.
Monochlorobenzene	C_6H_5Cl	276·8	136	—40	—40
Dichlorobenzene	$C_6H_4Cl_2$	339·8	171	+127·4	+53
Trichlorobenzene	$C_6H_3Cl_3$	402·8	206	62·6	17
Tetrachlorobenzene	$C_6H_2Cl_4$	464·0	240	282·2	139
Pentachlorobenzene	C_6HCl_5	521·6	272	185·0	85
Hexachlorobenzene	C_6Cl_6	618·8	326	438·8	226
Monobromobenzene	C_6H_5Br			302·0	150
Dibromobenzene	$C_6H_4Br_2$			417·2	214
Tribromobenzene	$C_6H_3Br_3$	527·0	275	111·2	44
Tetrabromobenzene	$C_6H_2Br_4$				
[The iodobenzenes are similar to the above.]					
Nitrobenzene .. .. (Artificial oil of almonds.)	$C_6H_5NO_2$				
Dinitrobenzene	$C_6H_4(NO_2)_2$				

The chlor-benzenes are formed by passing chlorine into a solution of iodine in benzene, the iodine acting as a carrier of the chlorine to the benzene.

The haloid substitution derivatives of benzene are stable bodies. Unlike the paraffin derivatives, they are unaffected by nascent hydrogen, or even by fusion with potassic hydrate. With hypochlorous acid, benzene forms the additive compound $C_6H_6(ClOH)_3$, which, by the action of water, forms a non-fermentable body called "*phenose*" ($C_6H_{12}O_6$), isomeric with grape-sugar. When this body is dissolved in fuming nitric acid, and water added to the solution, *nitrobenzene* ($C_6H_5NO_2$), or artificial essence of bitter almonds, separates, which, by the action of reducing agents, yields *aniline.*

Toluene.—*Methyl-benzene* ($C_7H_8 = C_6H_5.CH_3$). [*Molecular weight*, 92. *Boils at* 230° F. (110° C.). *Not solid at* —4° F. (—20° C.). *Specific gravity*, 0·881 at 41° F. (5° C.).]

Preparation.—(1.) From coal tar oil. It is contained in that portion which distils over between 212° and 248° F. (100° and 120° C.).

(2.) By the action of sodium on a mixture of bromobenzene and methyl iodide :—

$$\underset{\text{Bromobenzene}}{C_6H_5Br} + \underset{\text{Methyl iodide}}{CH_3I} + \underset{\text{Sodium}}{Na_2} = \underset{\text{Sodic bromide}}{NaBr} + \underset{\text{Sodic iodide}}{NaI} + \underset{\text{Toluene.}}{C_6H_5.CH_3}$$

(3.) By the action of methane in a nascent state on benzene.

Properties.—A limpid liquid. Chemically, behaves very like benzene, yielding benzoic acid when treated with oxidizing agents. Toluene being a mono-derivative of benzene, has no isomer.

Two isomeric derivatives are formed in almost every case by the action of reagents on toluene.

SERIES VI.—*Formula* C_nH_{2n-8}.

This includes:—

		Boiling point.		
		° F.	° C.	
Cinnamene .. .. (Styrolene or Phenylethylene)	C_8H_8	293	145	*Preparation.*—(1.) By passing the vapors of benzene and acetylene, or (2.) of benzene and ethylene, through a red-hot tube. (3.) By heating acetylene ($4C_2H_2 = C_8H_8$). (4.) Present in, and may be obtained from, liquid storax (*Liquid anibar orientale.*) *Properties.*—A colorless liquid. Does not solidify at —4° F. (—20° C.). Heated in closed tubes to 392° F. (200° C.) is converted into a white solid *metacinnamene*, which yields, on distillation, liquid *cinnamene*. Sp. gr. 0·924.
Allylbenzene ..	C_9H_{10}	338	170	*Preparation.*—By the action of nascent hydrogen on cinnamic alcohol.
Phenylbutylene ..	$C_{10}H_{12}$			*Preparation.*—By the action of sodium on a mixture of benzylic chloride and allylic iodide.

SERIES VII.—*Formula* C_nH_{2n-10}.

This includes,

Acetenylbenzene (C_8H_6) a colorless liquid boiling at 282·2° F. (139° C.). It is prepared by the action of an alcoholic solution of potassic hydrate on cinnamene dibromide ($C_8H_8Br_2 + 2KHO = C_8H_6 + 2KBr + 2H_2O$). Like acetylene, it precipitates many metallic solutions (page 275), forming such compounds as $(C_8H_5)_2Cu_2$, etc.

The Naphthalene Series.

SERIES VIII.—*Formula* C_nH_{2n-12}.

This includes,

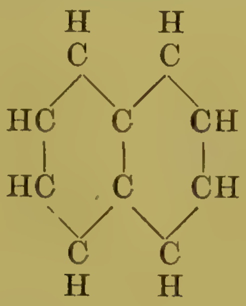
		Boiling point.	
		° F.	° C.
Naphthalene	$C_{10}H_8$	413·6	212
Methyl naphthalene	$C_{11}H_{10} = C_{10}H_7(CH_3)$	447·8	231
Ethyl naphthalene	$C_{12}H_{12} = C_{10}H_7(C_2H_5)$	483·8	251

Naphthalene ($C_{10}H_8$).

Occurrence and Preparation.—(1.) Naphthalene is a bye-product occurring in the preparation of coal gas. The latter portion of the distillate from coal tar yields a large quantity. It is produced whenever organic matters are distilled at a high temperature out of contact with air, or by the passage of the vapors of benzene, cinnamene, chrysene, anthracene, etc., through a red-hot tube.

(2.) By passing the vapor of dibromophenylbutylene over red-hot lime ($C_{10}H_{12}Br_2 = C_{10}H_8 + H_2 + 2HBr$).

Constitution.—From the formation and reactions of its substitution derivatives, the naphthalene molecule is assumed to consist of two benzene residues having two carbon atoms in common. Thus—



Properties.—(*a.*) *Physical.* A white solid body, crystallizing in brilliant scales. Has a faint narcissus-like odor. Melts at 176° F. (80° C.) and boils at 413·6° F. (212° C.). Its vapor density is 4·528. It is insoluble in cold water, slightly soluble in boiling water, very soluble in alcohol, in ether, in acetic acid, and in the volatile oils.

(*β.*) *Chemical.* It burns in air with a red smoky flame. It forms with chlorine and with bromine both additive and substitution compounds, such as $C_{10}H_8Cl_4$ and $C_{10}H_7Cl$, etc. By oxidation it yields *dinaphthyl*, $C_{20}H_{14}$, and *phthalic acid*, $C_8H_6O_4$. It is soluble in strong sulphuric acid, forming two isomeric *naphthalene-sulphonic acids* $C_{10}H_7(HSO_3)$, both of which form soluble baric salts. Nitric acid converts it, first, into a crystalline solid *nitronaphthalene* $C_{10}H_7NO_2$, and finally into *tetranitronaphthalene* $C_{10}H_4(NO_2)_4$. With a solution of chromic anhydride in acetic acid, it forms *naphtho-quinone* $C_{10}H_6O_2$.

SERIES IX.—*Formula* C_nH_{2n-14}.

This includes :—

		Melting point.		Boiling point.		
		° F.	° C.	° F.	° C.	
$C_{12}H_{10}$	Diphenyl.. .. .. (C_6H_5,C_6H_5)	140·0	60·0	464·0	240·0	*Preparation.*—By passing benzene through a red-hot tube ($2C_6H_6=C_{12}H_{10}+H_2$). By oxidation, forms *benzoic acid*. It sublimes at 140° F. (60° C.). It is contained in coal-tar, and distils over in that portion that boils between 518° and 572° F. (270° and 300° C.). By oxidation, forms *naphthalic acid*, which, when distilled with lime, yields *naphthalene*.
	Acenaphthene.. ..	203·0	95·0	514·4	268·0	
$C_{13}H_{12}$	Diphenyl methane.. (Benzyl benzene) (C_6H_5,CH_2,C_6H_5)	79·7	26·5	501·8	261·0	*Preparation.* — By the action of heat on a mixture of benzylic chloride and benzene ($C_6H_6+C_7H_7Cl=HCl+C_{13}H_{12}$). [The presence of a little zinc and copper facilitate the action.] By oxidation it yields *benzophenone* ($C_6H_5.CO.C_6H_5$).
$C_{14}H_{14}$	Ditolyl (*α*)	249·8	121·0			*Preparation.* — By the action of sodium on benzylic chloride. It is insoluble in water, but is soluble in alcohol and ether.
	,, (*β*)	liq	uid			
	($CH_3.C_6H_4C_6H_4.CH_3$)					
	Dibenzyl.. .. .. ($C_6H_5.CH_2.CH_2.C_6H_5$)	125·6	52·0	543·2	284·0	
	Benzyltoluene	liq	uid	534·2	277·0	
$C_{15}H_{16}$	Benzyl ethylbenzene	liq	uid	561·2	294·0	
	Benzyl metaxylene..	liq	uid	563·0	295·0	
	Benzyl paraxylene..	liq	uid	561·2	294·0	

Excepting acenaphthene, all these bodies act as saturated molecules, and form substitution but not additive compounds.

The Anthracene Series.

SERIES X.—*Formula* C_nH_{2n-18}.

This includes :—

		Melting point.		Boiling point.	
		° F.	° C.	° F.	° C.
Anthracene	$C_{14}H_{10}$	415·4	213	680	360
Amethylanthracene	$C_{16}H_{14}$				

Anthracene (*Paranaphthalene*). ($C_{14}H_{10}$.) *Molecular weight*, 178. *Specific gravity*, 1·147. Melts at 415·4° F. (213° C.); boils at 680° F. (360° C.).

Preparation.—(1.) Obtained commercially from the semi-solid portion of the coal-tar distillate, which comes over at from 644° to 752° F. (340° to 400° C.). It is important to note that when distilled *at the lower temperature*, the anthracene is more or less mixed with naphthalene, and that when distilled *at the higher temperature* it is mixed with chrysene and pyrene, these being the final products of the distillation of coal tar. Inasmuch, however, as anthracene is a valuable commercial product used in the preparation of artificial alizarine, and that alizarine cannot be produced either from naphthalene or from chrysene, the exact relation of anthracene to these bodies becomes important.

(2.) By passing benzene, mixed either with (α) ethylene, (β) with cinnamene, or (γ) with naphthalene vapor, through a red-hot tube:—

(α.) $2C_6H_6 + C_2H_4 = 3H_2 + C_{14}H_{10}$.
Benzene + Ethylene = Hydrogen + Anthracene.

(β.) $C_6H_6 + C_8H_8 = 2H_2 + C_{14}H_{10}$.
Benzene + Cinnamene = Hydrogen + Anthracene.

(γ.) $3C_6H_6 + C_{10}H_8 = 3H_2 + 2C_{14}H_{10}$.
Benzene + Naphthalene = Hydrogen + Anthracene.

(3.) By the action of heat on a mixture of (α) ethelyne and diphenyl, or (β) of ethylene and chrysene:—

(α.) $C_2H_4 + C_{12}H_{10} = 2H_2 + C_{14}H_{10}$.
Ethylene + Diphenyl = Hydrogen + Anthracene.

(β.) $C_2H_4 + C_{18}H_{12} = C_6H_6 + C_{14}H_{10}$.
Ethylene + Chrysene = Benzene + Anthracene.

(4.) By the action of heat on toluene, xylene, or cumene.

(5.) By the action of heat on benzylic chloride:—

$4C_7H_7Cl = C_{14}H_{10} + C_{14}H_{14} + 4HCl$.
Benzylic chloride = Anthracene + Benzyltoluene + Hydrochloric acid.

(6.) By the action of heat on a mixture of alizarine and zinc dust. Probably some of the alizarine is decomposed and hydrogen set free. The action may be formulated thus:—

$C_{14}H_8O_4 + H_2 + 4Zn = C_{14}H_{10} + 4ZnO$.
Alizarine + Hydrogen + Zinc = Anthracene + Zinc oxide.

Properties.—(*a.*) *Physical.* A colorless solid, crystallizing in four or six-sided plates. Specific gravity, 1·147. It sublimes at 212° F. (100° C.); melts at 415·4° F. (213° C.), and boils at 680° F. (360° C.). [Naphthalene melts at 176° F. (80° C.), and boils at 413·6° F. (212° C.).] Anthracene is insoluble in water, almost insoluble in cold alcohol (in which naphthalene is soluble), somewhat soluble in carbon disulphide and in boiling alcohol; soluble in ether, in benzene, and in the volatile oils (such as turpentine). Sunlight in time effects its physical transformation into *paranthracene*, a body that melts at 471·2° F. (244° C.). Paranthracene may be reconverted by fusion into common anthracene.

The molecule of anthracene is generally represented as consisting of two benzene residues united by the unsaturated hydrocarbon group C_2H_2, viz., $C_6H_4.C_2H_2.C_6H_4$.

(β.) *Chemical.*—With nascent hydrogen, anthracene forms a dihydride, $C_{14}H_{10},H_2$. With the haloids it forms both substitution and additive products.

Its reaction with oxidizing bodies is of great importance, inasmuch as by this means artificial alizarine, a product of great commercial value, identical with the red coloring matter of madder, is prepared. The equations representing the reactions that occur in its preparation may be thus stated :—

(1.) (α.) Heated with nitric acid, or with potassic bichromate and sulphuric acid, *anthracene* forms *anthraquinone*. Thus :—

$$2C_{14}H_{10} + 3O_2 = 2[C_{14}H_8(O_2)''] + 2H_2O.$$

Anthracene + Oxygen = Anthra-quinone + Water.

[N.B. In anthraquinone it will be noted that (O_2), like (Hg_2) in mercurous compounds, plays the part of a dyad radical.

This body is called anthraquinone because it bears the same relationship to anthracene that quinone bears to benzene. Thus :—

$$C_6H_6 — C_6H_4(O_2)''; \quad C_{14}H_{10} — C_{14}H_8(O_2)''.$$

Benzene — Quinone; Anthracene — Anthraquinone.]

(β.) When anthraquinone is heated with bromine it forms dibromanthraquinone. Thus :—

$$C_{14}H_8O_2 + 2Br_2 = C_{14}H_6Br_2O_2 + 2HBr.$$

Anthra-quinone + Bromine = Dibrom-anthra-quinone + Hydrobromic acid.

(γ.) When dibrom-anthra-quinone is heated to 350° F. (176·1° C.) with potassic hydrate, it forms the potassic derivative of dioxy-anthraquinone (or alizarin). Thus :—

$$C_{14}H_6Br_2O_2 + 4KHO = C_{14}H_6O_2(KO)_2 + 2KBr + 2H_2O.$$

Dibrom-anthra-quinone + Potassic hydrate = Potassic alizarate + Potassic bromide + Water.

(δ.) When an acid is added to a solution of the fused mass containing potassic alizarate, crude alizarin, $C_{14}H_8O_4$ or $C_{14}H_6(OH)_2(O_2)''$, is thrown down as a yellow precipitate, which when carefully sublimed produces a red sublimate of pure alizarin.

Alizarin may also be prepared as follows :—

(2.) (α.) By the action of chlorine on anthracene, when dichloranthracene is formed. Thus :—

$$C_{14}H_{10} + 2Cl_2 = C_{14}H_8Cl_2 + 2HCl.$$

Anthracene + Chlorine = Dichlor-anthracene + Hydrochloric acid.

(β.) In heating dichlor-anthracene with sulphuric acid, it forms dichlor-anthracene-disulphonic acid [$C_{14}H_6Cl_2(HSO_3)_2$]. Thus:—

$$C_{14}H_8Cl_2 + 2H_2SO_4 = C_{14}H_6Cl_2(HSO_3)_2 + 2H_2O.$$

Dichlor-anthracene + Sulphuric acid = Dichlor-anthracene disulphonic acid + Water.

(γ.) By the action on this product of oxidizing agents, or by heating it with strong sulphuric acid, it forms anthraquinone-disulphonic acid $C_{14}H_6O_2(HSO_3)_2$. Thus:—

$$C_{14}H_6Cl_2(HSO_3)_2 + O_2 = C_{14}H_6O_2(HSO_3)_2 + Cl_2.$$

Dichloranthracene disulphonic acid + Oxygen = Anthra-quinone-disulphonic acid + Chlorine.

(δ.) When this is heated with potassic hydrate it forms potassic alizarate, which is then treated with an acid in the manner already described.

$$C_{14}H_6O_2(HSO_3)_2 + 6KHO = C_{14}H_6O_2(KO)_2 + 2K_2SO_3 + 4H_2O.$$

Anthra-quinone-disulphonic acid + Potassic hydrate = Potassic alizarate + Potassic sulphite + Water.

Alizarin is soluble in alkaline solutions, and in solutions of the alkaline carbonates, forming deep purple liquids, from which alizarin may be precipitated by an acid.

Coal tar oil contains several isomers of anthracene. For example, *phenanthrene*, a solid, melting at 212° F. (100° C.), and boiling at 644° F. (340° C.); *tolane*, a solid, melting at 140° F. (60° C.); and a third body melting at 476·6° F. (247° C.), have been prepared.

NOTE.—We may here note, that, starting from benzene, we have a complete series of hydrocarbons, where the successive terms differ by C_4H_2. Thus:—

	Formulæ.	Fusing point.		Boiling point.	
		° F.	° C.	° F.	° C.
Benzene	C_6H_6	41·9	5·5	176·9	80·5
Naphthalene	$C_{10}H_8$	176·0	80·0	413·6	212·0
Anthracene	$C_{14}H_{10}$	415·4	213·0	680·0	360·0
Chrysene	$C_{18}H_{12}$	478·4	248·0		

The relationship of these bodies is remarkable. They all form *Quinones* (that is, bodies where H_2 is replaced by $(O_2)''$) *directly* (in all cases except that of benzene) as products of their oxidation (*see* page 624). These quinones are neutral bodies, and furnish hydro-quinones (the dioxy-derivatives of the several hydrocarbons), by the action of nascent hydrogen. Thus:—

$$C_6H_6 \;—\; C_6H_4(O_2)'' \;—\; C_6H_4(OH)_2.$$

Benzene — Quinone — Hydroquinone.

SERIES XI.—*Formula* C_nH_{2n-16}.

This includes only *stilbene* or *toluyene* ($C_{14}H_{12}$). This hydrocarbon is a crystalline solid, prepared by the action of heat on dibenzyl ($C_{14}H_{14}=C_{14}H_{12}+H_2$). It melts at 212° F. (100° C.), and boils at 557·6° F. (292° C.). It forms both substitution and additive products. *Tolane* ($C_{14}H_{10}$) is formed by the action of potassic hydrate on the dibromide $C_{14}H_{12}Br_2$.

SERIES XII.—*Formula* C_nH_{2n-22}.

This includes—

		Fusing point.		
		° F.	° C.	
$C_{16}H_{10}$	Diacetenylbenzene Pyrene $C_{10}H_6(C_6H_4)$	287·6	142·0	Present in coal-tar oil. (N.B.—These bodies contain 95 per cent. of carbon.)
$C_{18}H_{14}$	Diphenylbenzene $C_6H_4(C_6H_5)_2$	401·0	205·0	Obtained, with other products, by passing benzene through red-hot tubes. It yields an oxidation, first *phenylbenzoic* acid $C_6H_5C_6H_4(CO_2H)$, and finally *terephthalic* acid $C_6H_4(CO_2H)_2$.
$C_{19}H_{16}$	Triphenylbenzene $CH(C_6H_5)_3$	198·5	92·5	*Preparation.*—By the action of heat in closed tubes on a mixture of benzylene chloride, and mercuric phenyl.

SERIES XIII.—*Formula* C_nH_{2n-24}.

Chrysene ($C_{18}H_{12}$). This, the only known member of the series, is found together with pyrene ($C_{16}H_{10}$) as the final product of the distillation of coal tar. It crystallizes in fine yellow scales, which melt at from 473° to 478·4° F. (245° to 248° C.). It is insoluble in alcohol, and nearly insoluble in ether, but is soluble in boiling turpentine, from which it is deposited as the liquid cools. By oxidation it forms *chrysoquinone* ($C_{18}H_{10}O_2$).

SERIES XV.—*Formula* C_nH_{2n-32}.

This includes *tetraphenylethylene* ($C_2(C_6H_5)_4=C_{26}H_{20}$), a crystalline body which melts at 428° F. (220° C.), and is prepared by the action of heat on a mixture of finely divided silver and benzophenonic chloride, this latter body being a product of the action of phosphorus pentachloride on diphenyl ketone. Thus :—

$2[(C_6H_5)_2CCl_2]$	+	$2Ag_2$	=	$C_2(C_6H_5)_4$	+	$4AgCl$.
Benzophenonic chloride	+	Silver	=	Tetraphenylethylene	+	Argentic chloride.

SUPPLEMENT TO CHAPTER ON THE HYDROCARBONS.

ADDENDUM TO THE PARAFFINS.

Petroleum—Paraffins.

The paraffins, it will be noted, vary greatly in their physical conditions. The higher terms are *solid*, and are employed in the manufacture of candles, etc. A series of *buttery* compounds, used for lubricating purposes, succeed. Then follow compounds which are *liquid*, and are used for burning in lamps ; and, finally, certain liquids volatile below 100° F. (37·8° C.) (*petroleum spirit*), that are used as solvents in the arts.

In *American petroleum* and in the mineral oils of a like nature found in or near the coal formation, and formed by the gradual decomposition of vegetable matter beneath the earth's surface, we have an admixture of numerous hydrocarbons of this group of paraffins. In order to prepare the oil for illuminating purposes, it is necessary that the hydrocarbons volatile at a temperature above 100° F. (37·8° C.), (that is, all the hydrocarbons containing less than six carbon atoms), should be distilled off, otherwise the oil might be dangerous. This distillate constitutes what is called "*Petroleum spirit,*" and is used as a solvent for caoutchouc, resinous bodies, etc., whilst the liquid remaining in the retort (called *petroleum oil*) is safe for burning in lamps.

Paraffin oil, which is also a mixture of the paraffin hydrocarbons, is obtained by the destructive distillation of such bodies as boghead cannel, peat, etc. The most volatile portions are used for illuminating purposes, the least volatile (mixed with fatty oils, such as rape, cotton, etc.) being employed for lubricating machinery.

Paraffin.

If petroleum (Rangoon tar or rock oil), or paraffin oil be subjected to an intense cold, the separation of a solid body, called *paraffin*, takes place. This substance exists ready formed in such minerals as ozokerit, mineral wax, etc. It is a compound of several hydrocarbons of the CH_4 group, and is largely used for candles, etc. The following is an outline of its preparation :—

The crude tar resulting from the destructive distillation of boghead cannel, etc., is distilled. The distillate is first shaken up with a sodic hydrate solution in order to remove all acid bodies. It is afterwards treated with sulphuric acid, to remove all basic substances, such as naphthalene, etc. The residue of these operations, after being well washed, is distilled, and the solid distillate collected. And liquid oils present in the mass are now extracted, first by a centrifugal apparatus, then by pressure in the cold, and finally by pressure at or about 105° F. (40·5° C.), so as to remove all hydrocarbons melting below this temperature. The residue is again treated with sulphuric acid, whereby all hydrocarbons other than paraffins are charred. The paraffin collects on the surface of the acid, and may be removed. After washing, it is melted in oils of low boiling-point, the solution decolorised by filtration through animal charcoal, and finally the volatile oils removed by distillation from the pure paraffin.

Properties.—(*a.*) *Physical.* A white waxy solid, without taste or smell. Its fusing-point varies, according to its source, from 104° F. (40° C.) to 140° F. (60° C.), the latter being the temperature at which the paraffin obtained from ozokerit melts. It boils at about 698° F. (370° C.). A continuous heat under pressure converts it into liquid hydrocarbons (Thorpe and Young). It is insoluble in water, slightly soluble in alcohol, very soluble in ether, in bisulphide of carbon, and in the fixed and volatile oils.

(*β.*) *Chemical.*—Paraffin is remarkable, as its preparation given above would indicate, for its resistance to most chemical reagents (*parum affinis*). When, however, it is heated continuously for several days with sulphuric acid and potassic dichromate, cerotic acid is formed ($C_{27}H_{54}O_2$), and when similarly treated with nitric acid, a mixture results of solid and liquid fatty acids. When melted paraffin is acted on with chlorine, it is gradually attacked, hydrochloric acid being evolved.

ADDENDUM TO THE "TURPENES."

Oil of Turpentine and its Allies.—The Turpenes.

The name *turpentine* is given to an oleo-resinous juice exuding from certain varieties of pines. *Common English turpentine* is obtained from the Scotch fir, the Pinus Australis and Pinus Tœda ; *Venice turpentine* from the larch ; *French turpentine* from the Pinus maritima, etc.

"Turpentine" is a solution of rosin in spirits of turpentine. When distilled, the residue in the retort, amounting to from 75 to 90 per cent., constitutes *rosin,* and the distillate, varying in quantity from 10 to 25 per cent., constitutes *turps*, or *spirits of turpentine.* In the case of the Boston turpentine, the distillate constitutes "camphine."

Properties of spirits of turpentine.—(*a.*) *Physical.* A colorless, mobile, peculiar smelling liquid. Sp. gr. 0·864. It boils at 320° F. (160° C.).

It is not very soluble in water, but is very soluble in alcohol, carbonic disulphide, and in ether, and is itself a solvent for iodine, sulphur, phosphorus, resinous and fatty matters, caoutchouc, etc. It is a powerful refractor of light.

(β.) *Chemical.* When *French spirits of turpentine* is neutralised with an alkaline carbonate and distilled, it yields "terebenthene" ($C_{10}H_{16}$), a liquid boiling at 321·8° F. (161° C.), and having a sp. gr. of 0·864. It turns the plane of polarisation *to the left. English spirits of turpentine* similarly treated, yields "austraterebenthene," a liquid having a similar gravity and boiling-point to terebenthene, but turning the plane of polarisation *to the right.*

(1.) Both bodies (*i.e., terebenthene* or *austraterebenthene*) when heated to 482° F. (250° C.) form two *levo-rotatory* oils, which may be separated by distillation ; viz., *austrapyrolene*, boiling at 352·4° F. (178° C.), and *metaterebenthene* ($C_{20}H_{32}$), boiling at 680° F. (360° C.).

(2.) By the action of air, turpentine becomes oxidized and forms a product of a resinous nature.

(3.) Spirits of turpentine, though insoluble in water, forms three hydrates : viz., (α) a crystalline hydrate, $C_{10}H_{16},3H_2O$, soluble in water, and fusing at 217° F. (102·8° C.) ; (β) a second crystalline hydrate, $C_{10}H_{16},2H_2O$, subliming at 480·9° F. (248° C.) formed by the action of heat on the former hydrate ; and (γ) a liquid hydrate called *terpinole*, $(C_{10}H_{16})_2,H_2O$, having an odor of hyacinths, and obtained by distilling either of the former hydrates with sulphuric acid.

(4.) *Chlorine* and *bromine* are so rapidly absorbed by turpentine, that combustion frequently results, HBr and HCl being formed, and carbon set free. Distilled with water and chloride of lime, chloroform is formed. With *iodine*, combustion does not usually occur. The solution of iodine in turpentine is green, and, as the heat increases during the progress of the chemical action, hydrochloric acid is evolved.

(5.) By the action of gaseous boric fluoride, or when the spirits of turpentine is digested with a little oil of vitriol in the cold, it yields two liquids, both of which are without action on a polarised ray ; viz., *terebene* ($C_{10}H_{16}$), a liquid boiling at 320° F. (160° C.), having the odor of thyme, and *colophene* or *diterebene* ($C_{20}H_{32}$), a liquid boiling at 600° F. (315·5° C.), and having a sp. gr. of 0·940 (vapor density 4·76). This latter liquid appears colorless by directly transmitted light, and blue by obliquely transmitted light. Both terebene and colophene are a mixture of hydrocarbons.

(6.) *Common nitric acid* forms, with turpentine, acid products. The action of the fuming acid upon it is sufficiently energetic to cause combustion.

The following volatile or essential oils have the same composition as common spirits of turpentine ($C_{10}H_{16}$), viz., oils of lemon, orange, bergamot, lime, citron, neroli (?), caraway, camomile, coriander, elemi, gomart, hop, juniper, laurel, parsley, savin, thyme, valerian, wintergreen, cloves, etc. The oils of copaiba and cubebs ($C_{20}H_{32}$) are also polymeric with spirits of turpentine.

All these bodies form resinoid substances by exposure to air. They also form crystalline hydrates and artificial camphors, by the action of hydrochloric acid.

It will be convenient here to consider a few bodies, the exact relationship of some of which it is not easy to define.

I. Essential or Volatile Oils.

These hydrocarbons are found for the most part in the vegetable kingdom and in all parts of the plant: sometimes in the *seed*, as in the mustard; sometimes in the *rind of the fruit*, as in the orange; sometimes in the *flower*, as in the rose; sometimes in the *leaves*, as in the myrtle. A few only are found in the bodies of animals, such as *e.g.*, the oil of ants.

Preparation of the Volatile Oils.—(α.) By *pressure*. *Examples*—Oils of lemon, bergamot, laurel, etc.

(β.) By *distillation* with water. This is the common method of extracting the majority of these oils.

(γ.) By *fermentation and distillation*. This is illustrated in the preparation of the oils of bitter almond and mustard, where, after the seed has been crushed and mixed with water, the action of some nitrogenized body on certain compounds in the seed, develops the oil which is afterwards extracted by distillation.

(δ.) By *destructive distillation*. *Examples.*—The volatile oils from peat, wood, coal, bones, etc.

(ε.) By *solution in a fixed oil* destitute of odor (such as poppy oil). *Examples*—Oils of geranium, jessamine, violet, heliotrope, etc.

(ζ.) By *chemical action*. *Example*—Oil of spiræa, from salicine.

Properties.—(α.) *Physical*. At ordinary temperatures these oils are usually liquid. Oil of aniseed, however, is a solid. Their color is mostly yellow when first prepared, but they rapidly darken by exposure to air from absorption of oxygen, becoming finally a resinoid mass. Their odor is powerful. Their boiling-point is usually above 212° F. (100° C.). They produce on paper a greasy stain *which is transient*, and dissipated by heat. Their specific gravities vary, but they are usually lighter than water.

(β.) *Chemical*. They are all combustible bodies, slightly soluble in water, the solution forming the officinal medicated waters. They are freely soluble in spirit (forming essences), from which solutions they are precipitated by water. They are soluble in fatty oils. By the action of cold they separate into a solid crystalline compound (camphor or stearoptene) and a liquid oil (elœoptene). They are destroyed by the action of acids. They are insoluble in potash, and are not saponified by alkalies.

Essential Oils.

ISOMERS OF TURPENTINE.

ls of	Specific Gravity.		Boiling Pt.		Direction of Rotation.	Source.	Remarks.
	Liquid.	Vapor.	° F.	° C.			
T tine ..	0·864	4·812	320	160·0	left	Coniferous trees.	
B iot ..	0·869		361	182·8	right		See Oil of Lemon.
B ne		4·60	320	160·0	left		
B	0·847	5·28	313	156·1			
C ile ..			347	175·0		Anthemidis flores	Contains the hydrocarbon $C_{10}H_{16}$, and an oxidized body, $C_{10}H_{16}O_2$.
C y	0·938	5·17	343	172·8	right		Contains *carvene* ($C_{10}H_{16}$) and *carvol* ($C_{10}H_{14}O$).
C	0·918		289	142·8			
E	0·849		345	173·9	left		
H					right		
J r	0·86		320	160·0	left		
L	0·851	4·87	343	172·7	right		Contains, in common with many others, *hesperidene* ($C_{10}H_{16}$), and certain oxidized hydrocarbons.
O	0·83	4·64	356	180·0	right		See Lemon.
P			320	160·0			
P	0·864	4·73	333	167·2			
S			320	160·0			
T	0·837		320	160·0			
T		4·76	329	165·0	none		
C	0·878		500	260·0	left		} $C_{15}H_{24}$.
C	0·929		490	254·5	left		
A of Roses .			592	311·1			Contains a solid hydrocarbon, C_8H_{16}, and an oxidized product, to which the scent is due.
B Almond .						Amygdala amara	
D						Fructus anethi	Contains *anethene* ($C_{10}H_{16}$), and an oil $C_{10}H_{14}O$.
A 1						Pompenella anisum	Contains a solid hydrocarbon, $C_{10}H_{16}$.
H adish ..							*Composition*, C_4H_9CNS.
N							See Oil of Lemons.
C ioms ..							Ditto. It also contains a camphor, $C_{10}H_{16}3H_2O$.
C							Contains *cajuputol* ($C_{10}H_{16}.H_2O$).
C ion ..	1·050						
F							
P mint ..							Contains *menthene* ($C_{10}H_{18}$).
S as	1·094						
W d	1·015						

II. Camphors.

Camphors are oxidized hydrocarbons, and are closely related to the essential oils.

Common camphor ($C_{10}H_{16}O$) is obtained from the wood of the Laurus Camphora, or camphor laurel, by boiling it in water, and condensing the camphor as it passes over, on straw placed at the head of the still. It is afterwards purified by sublimation. An oil distils over during the action, called *liquid camphor* or *oil of camphor* $(C_{10}H_{16})_2O$, which by exposure to air oxidizes and deposits common camphor.

Properties.—(a.) Physical. A white crystalline (octahedra) solid, volatile at ordinary temperatures. It has a specific gravity of 0·996. It fuses at 347° F. (175° C.), and boils at 399° F. (203·9° C.). It rotates a ray of light to the right (+47·4). It is very slightly soluble in water (1 in 2,000 parts, or 40 grains per gallon), but is freely soluble in alcohol, in ether, in chloroform, and in strong acetic acid.

(β.) *Chemical.* Camphor burns with a smoky flame. When distilled it yields the colorless compound *camphoric oxide* ($C_{10}H_{14}O_3$). Distilled with P_2S_5 or with phosphoric anhydride, it forms *cymene* and *hydrochloric acid.* With nitric acid it forms *camphoric acid* ($C_{10}H_{16}O_4$), a dextro-rotatory body. It is acted on by bromine, forming $C_{10}H_{16}Br_2O$. Other bromine compounds also may be formed, such as *monobromcamphor* ($C_{10}H_{15}BrO$). Chlorine is without action upon it. Heated in sealed tubes with an alcoholic solution of caustic soda, it is resolved into *camphol* ($C_{10}H_{18}O$) and *camphic acid* ($C_{10}H_{16}O_2$).

Borneo camphor ($C_{10}H_{18}O$) is an exudation from the *Dryabalanops camphora.* It crystallizes in prisms. By distillation it yields a volatile oil called *borneène* ($C_{10}H_{16}$), which is often sold in the market as camphor oil, or liquid camphor.

By oxidation with nitric acid, Borneo camphor forms common camphor; whilst, by the action of metallic sodium on a solution of common camphor in toluene, it may be converted into Borneo camphor.

Common camphor rotates a ray of light to the right. The *camphor contained in the oil of feverfew* rotates it to the left. *The camphor in the essential oils* of the *N. O. Labiatæ* are optically inactive. The camphoric acids respectively formed from these camphors by the action upon them of nitric acid, have similar optical effects to the camphors themselves, but if the right and the left rotatory acids be mixed together in equal proportions, the compound acid formed is found to be without action on the polarized ray.

III. Resins.

Resins are bodies which exude from plants, dissolved in the essential oil peculiar to the plant. They are for the most part oxidized terebenes, and are produced in the plant by the oxidation of their essential oils.

Preparation.—(1.) By simple exudation. *Example*—Copal.

(2.) By distilling the oil from the resin in which it is dissolved. *Example*—Common rosin.

(3.) By destructive distillation. *Examples*—Guiacum, pitch.

Properties.—(*a.*) *Physical.*—The resins are solid transparent bodies, sometimes crystallizable. They have no well-marked odor. They are easily fused, but they are not volatile. They are decomposed when heated in closed vessels. They are insoluble in water, but are soluble in spirit. They are electrical insulators, and yield, by friction, negative electricity.

(β.) *Chemical.*—The resins are combustible, and burn with a white flame. Many of them are acid to litmus (as, *e.g.*, sandarach and guiacum), and yield a lather when acted on with an alkaline lye. This mixture, however, differs from a soap solution in not being precipitated on the addition of a solution of common salt.

The resins generally are compounds of more than one resin. Their exact proximate constitution is not, in the majority of cases, well understood.

Varieties of Resins.

Resins.	Sources.
Common rosin (*colophony*) Brown	The residue of American turpentine (*pinus abies*).
White	(Galipot). The residue of Bordeaux turpentine (*pinus maritima*).
Amber	A fossil resin.
Arnicin ($C_{20}H_{30}O_4$)	The active principle of arnica root (*arnica radix*).
Cannabin	Indian hemp (*cannabis indica*).
Capsicum resin	Obtained from the fruit of the capsicum.
Castorin	Castor is the dried preputial follicles and secretions of the beaver.
Copal	An exuded resin from certain extinct trees (*hymenæa verrucosa ?*). It is found beneath the ground.
Dammar resin	
Dragon's blood ($C_{20}H_{20}O_4$)	An exudation from the fruit of a palm (*calamus draco*).
Ergotin	An active constituent of ergot.
Guiacum resin	From the wood of *guiacum officinale.*
Jalap resin	From the jalap tubercles. It is insoluble in turpentine.
Koussin ($C_{31}H_{38}O_{10}$)	From kousso.
Lac	An exudation on certain trees (as the *ficus indica*) produced by the puncture of an insect (*coccus*).
Mastich	From the stem of the mastic or lentisk tree (*pistachia lentiscus*).
Mezereon resin	From the dried bark of the *Daphne mezereum.*
Burgundy pitch	From the stem of the spruce fir (*abies excelsa*).
Podophyllum resin	From podophyllum root.
Pyrethrin	From pellitory root.
Rhubarb resin	From rhubarb.
Rottlerin	From kamala.
Sandarach	From the *juniperus communis.*

1. *Common rosin* (colophony) is the residue of the distillation of turpentine. The quantity obtained varies from 75 to 90 per cent. of the turpentine employed. It is a mixture of two acid bodies, viz., a crystallizable acid called *abietic acid* ($C_{44}H_{64}O_5$), and an amorphous acid called *pinic acid* ($C_{20}H_{30}O_2$).

2. *Lac* is an exudation from certain trees, occasioned by the puncture of an insect. "*Stick lac*" is the crude state in which the resin is collected. "*Seed lac*" is the resinous residue left after boiling the crude lac with a solution of sodic carbonate, in order to extract from it a red-coloring matter (lac-dye) used by the dyer. *Shellac*" is the fused "seed lac." This resin is largely used for hats, sealing-wax, and varnishes. "*Indian ink*" consists of a mixture of shellac (100 grs.), borax (20 grs.), lampblack and water (4 ozs.). "*Lacquer*" is an alcoholic solution of shellac, sandarach, and Venice turpentine.

3. *Amber* is a fossil resin found accompanying lignite. It is soluble in alcohol (1 part in 8), and in ether (1 in 10). It is more soluble in these liquids after it has been fused than before. When acted on with nitric acid or digested with alkalies, it yields succinic acid.

4. *Copal* differs from other resins by its comparatively slight solubility in alcohol and in essential oils. When melted, however, it mixes with oils, and is thus made into varnish.

5. *Guiacum resin* is the exudation from the wood of the guiacum officinale. It is soluble in alcohol. Oxidizing agents, under the influence of certain organic substances, produce a blue, green, and brown color with the alcoholic solution.

Uses of Resins.—For varnishes. For stiffening purposes; for yellow soap, and for sealing-wax.

In the manufacture of varnishes, the powdered resin (copal, mastic, sandarach, lac, elemi and anime being those most frequently used) is mixed with some powdered glass, so as to prevent its becoming lumpy. The solvents principally employed are turpentine, methylated alcohol and wood spirit. In the case of copal, mastic and sandarach, certain liquids such as acetone, a little turpentine or some fixed oil (such as linseed or poppy), are commonly added to prevent the varnish cracking when dry (oil varnishes). Spirit varnishes dry rapidly; oil varnishes dry slowly, but are more durable.

IV. Gum Resins.

Definition.—Mixtures of a resin or of an oleo-resin with a gum.

Gum resins form an emulsion when rubbed up with water, *i.e.*, the particles of resin are held in suspension by the solution of gum. The gum resins are soluble in dilute alcohol and in weak alkalies. They form a numerous class, amongst which may be mentioned ammoniacum, assafœtida, aloes, euphorbium, galbanum, gamboge, myrrh, olibanum or Arabian frankincense, and scammony.

V. Oleo-Resins.

Definition.—A mixture of a resin and a volatile oil.

This class includes copaiva, the turpentines, common frankincense, (Pinus Tœda), Canada balsam (the turpentine from the Balm of Gilead fir), sumbul root, etc.

VI. Balsams.

Definition.—A resin, or an oleo-resin, containing benzoic or cinnamic acid. (*Memo.* Balsam of Copaiba and Canada balsam are not true balsams, as they neither contain cinnamic nor benzoic acid.)

This class includes benzoin (styrax benzoin), balsam of Peru (myroxylon Pereira), balsam of tolu (myroxylon toluifera), storax (liquidambar orientale), etc.

India Rubber—Caoutchouc.

Natural History.—A milky juice, solidifying on exposure to air. It is obtained from many tropical plants, such as the *Ficus elastica*, etc.

Constitution.—A mixture of several isomers and polymers of turpentine oil.

Preparation.—The juice, which is perfectly white and liquid when first obtained, flows from incisions made in the tree, and is then dried on clay moulds.

Properties of the solid caoutchouc. — An elastic solid. Specific gravity 0·93. It melts at 250° F. (120·9° C.). When heated slightly beyond its melting-point, it forms a liquid which does not solidify on cooling. At a higher temperature it is decomposed into two liquids, viz., *isoprene* (C_5H_8), boiling at 98·6° F. (37° C.), and *caoutchine,* boiling at 339·8° F. (171° C.), and in both of which liquids caoutchouc is soluble. It is insoluble in alcohol or in water, but is softened by boiling water. It is soluble in ether, in naphtha, and in the volatile oils, and remains unchanged as the solvent evaporates. Neither alkalies, dilute acids, nor indeed chemical reagents generally, have any action upon it. It combines with about 2 to 3 per cent. of sulphur when melted in contact with it, forming "Vulcanized India Rubber," which is a more elastic body than rubber, but is insoluble in naphtha or in turpentine, and is incapable like rubber, of cohering to other surfaces with which it may be brought into contact.

Uses :—

1. For general cleansing purposes.
2. For waterproofing.
3. For *vulcanized India rubber.* Most specimens of vulcanized rubber contain more than 2 per cent. of sulphur. Under such circumstances the rubber after a short time becomes inelastic and brittle, owing to the oxidation of the free sulphur.
4. For *ebonite* (vulcanite). This is prepared by mixing caoutchouc with about half its weight of sulphur, and afterwards hardening the mixture by heat and pressure. It takes a high polish.
5. *Marine glue* is a solution of caoutchouc, mixed with a little shellac, in coal-tar naphtha.

Gutta Percha.

Natural History. — A milky juice exuding from the Isonandra percha, and solidifying by exposure to air.

Composition.—Similar to that of caoutchouc.

Properties.—An inelastic solid; specific gravity 0·98. It is insoluble in water, alcohol, acids or alkalies, but is soluble in ether, volatile oils, chloroform, carbonic disulphide, naphtha, etc. It softens at 212° F. (100° C.) and decomposes at 400° F. (204·4° C.). It may be vulcanized like caoutchouc.

CHAPTER XXIII.

THE ALCOHOLS.

Relation of Alcohols to other Bodies—Series of Alcohols—General Preparation and Properties of the Members of the various Series—Mercaptans.

SUPPLEMENTARY CHAPTER: Sugar — Glucosides — Starches—Gums — Reaction of various Alcohols and allied Bodies.

THE alcohols are saturated derivatives of the hydrocarbons, one or more atoms of the hydrogen of the hydrocarbon being replaced by a semi-molecule of hydroxyl (OH);—in other words, the alcohols are hydroxides analogous to the hydroxides of the metals.

(*a*.) If 1 hydrogen atom only of the hydrocarbon be replaced by 1 of the group (OH), a *monohydric alcohol* is formed. Thus $C_3H_7(OH)$, a derivative of C_3H_8, constitutes monohydric propylic alcohol.

(β.) If 2 or more hydrogen atoms be replaced by 2 or more of the group (OH), a *dihydric* (or trihydric, etc.) *alcohol* is formed. Thus $C_3H_5(OH)_3$ constitutes the trihydric alcohol glycerine.

The exact relationship of the alcohols to the ethers must be noted.

Relation of the alcohols to the haloid ethers.—If the group or groups of (OH) in the alcohol, be replaced (partly or wholly) by chlorine (*e.g.*, by the action upon the alcohol either of a haloid acid, or of a compound of phosphorus with a haloid), a *haloid ether* is formed. Thus *propylic alcohol*, $C_3H_7(OH)$, forms *propane chloride*, $C_3H_7(Cl)$.

If this haloid ether be treated with potassic or sodic hydrate, the alcohol will be reformed; thus:—

$C_3H_7(Cl)$	+	KOH	=	$C_3H_7(OH)$	+	KCl.
Propane chloride	+	Potassic hydrate	=	Propylic alcohol	+	Potassic chloride.

Relation of the alcohols to the oxy-ethers.—If the group or groups of (OH) in the alcohol be replaced by potassoxyl (OK) or methyloxyl (OCH_3), etc., an *oxygen ether* is formed. Thus—

Ethylic alcohol $C_2H_5(OH)$ forms $C_2H_5(OK)$, *potassic ethylate*;
" " $C_2H_5(OCH_3)$, *methylic ethylate*, etc.

Relation of the alcohols to the compound ethers (ethereal salts).—If the hydrogen of the hydroxyl (OH) in the alcohol, be replaced by an acid radical, an *ethereal salt* is formed. Thus—

Methylic alcohol, $CH_3(OH)$, forms $CH_3(C_2H_3O_2)$, *methylic acetate*.

Constitution.—An alcohol may be regarded as formed on the water type, where one atom of hydrogen is replaced by a compound hydrocarbon radical. Thus—

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O = \underset{\textit{Ethylic alcohol;}}{C_2H_5(OH)} \qquad \left.\begin{matrix}C_3H_7\\H\end{matrix}\right\}O = \underset{\textit{Propylic alcohol.}}{C_3H_7(OH)}$$

The alcohols may be arranged in the following groups :—

SERIES.	Formulæ.	Examples.
A.—MONOHYDRIC ALCOHOLS—		
I. Ethylic series	$C_nH_{2n+1}(OH)$	Methylic alcohol $CH_3(OH)$.
II. Vinylic series	$C_nH_{2n-1}(OH)$	Vinylic alcohol $C_2H_3(OH)$.
III.	$C_nH_{2n-3}(OH)$	Propargylic alcohol $C_3H_3(OH)$.
IV.	$C_nH_{2n-5}(OH)$	
V. Benzylic series	$C_nH_{2n-7}(OH)$	Phenol $C_6H_5(OH)$.
VI. Cinnamic series	$C_nH_{2n-9}(OH)$	Cinnamic alcohol $C_9H_9(OH)$.
VII.	$C_nH_{2n-13}(OH)$	
B.—DIHYDRIC ALCOHOLS—		
I. Glycols	$C_nH_{2n}(OH)_2$	Glycol $C_2H_4(OH)_2$.
II. Orcins	$C_nH_{2n-8}(OH)_2$	Orcin $C_6H_3(CH_3)(OH)_2$.
C.—TRIHYDRIC ALCOHOLS—		
I. Glyceric series	$C_nH_{2n-1}(OH)_3$	Glycerin $C_3H_5(OH)_3$.
II. Pyrogallic series ..	$C_nH_{2n-9}(OH)_3$	Pyrogallol $C_6H_3(OH)_3$.
D.—TETRAHYDRIC ALCOHOLS—	$C_nH_{2n-2}(OH)_4$	Erythrite $C_4H_6(OH)_4$.
E.—HEXHYDRIC ALCOHOLS—	$C_nH_{2n-4}(OH)_6$	Mannite $C_6H_8(OH)_6$.

A.—MONOHYDRIC ALCOHOLS.

Ethylic Series.

SERIES I.—*Formula* $C_nH_{2n+1}(OH)$.

This includes :—

Alcohols.	Formulæ.	Specific Gr. at ° C.	Boiling Pt.		Vapor Density.	Sources.
			° F.	° C.		
Methylic (wood naphtha)	$CH_3(OH)$	0·798 at 20	151·0	66·1	1·12	Destructive distillation of wood.
Ethylic (spirits of wine)	$C_2H_5(OH)$	0·7938 at 15	173·0	78·3	1·61	Fermentation of sugar.
Propylic	$C_3H_7(OH)$	0·8205 at 0	206·0	96·6	2·02	Ditto of grape husks.
Butylic	$C_4H_9(OH)$	0·8032 at 18	233·0	111·7	2·59	Ditto of beet root.
Amylic (fusel oil; pentylic)	$C_5H_{11}(OH)$	0·8111	269·8	132·1	3·15	Ditto of potatoes.
Hexylic (caproic) ..	$C_6H_{13}(OH)$	0·819 at 23	309·0	153·9	3·53	Ditto of grape husks.
Œnanthic (heptylic)	$C_7H_{15}(OH)$		343·0	172·8		Fermentation of grape husks.
Caprylic (octylic) ..	$C_8H_{17}(OH)$	0·8717 at 16	356·0	180·0	4·50	Distillation of castor oil with KHO.
Nonylic	$C_9H_{19}(OH)$		392·0	200·0		
Rutic (decatylic) ..	$C_{10}H_{21}(OH)$		414·0	212·2		Oil of rue.
Lauric	$C_{12}H_{25}(OH)$					Whale oil.
Cetylic (ethal) ..	$C_{16}H_{33}(OH)$					Spermaceti; fuses at 122° F.
Cerylic (cerotene) ..	$C_{27}H_{55}(OH)$					Chinese wax; fuses at 174° F.
Melissic (melissine)	$C_{30}H_{61}(OH)$					Beeswax; fuses at 185° F.

Isomeric forms.—All these alcohols (excepting the first two terms) have numerous isomeric modifications. They are distinguished partly by their different physical properties, such as by their different boiling-points, but more especially by their behaviour on oxidation. We are indebted to Kolbe for a systematic arrangement of these isomerides. To methylic alcohol ($CH_3.OH$) he has given the name *carbinol*, whilst all the succeeding alcohols he terms *carbinols*, regarding them as derivatives of the first term (methylic alcohol), and formed by the replacement of hydrogen by monad radicals of the form C_nH_{2n+1}:

(*a.*) If, judging by its preparation and by its mode of formation, the alcohol be formed by the replacement of 1 unit of hydrogen of the carbinol by the compound group (C_nH_{2n+1}), the alcohol is then called a *primary alcohol.* Thus, ($CH_3.OH$) being carbinol—

$CH_2(CH_3)OH$ is the primary alcohol *methyl carbinol* (ethylic alcohol).
$CH_2(C_2H_5)OH$,, ,, *ethylic carbinol* (propylic alcohol).

(*β.*) If two units of hydrogen of the carbinol be replaced by 2 of the group (C_nH_{2n+1}), the alcohol is then called a *secondary alcohol.* Thus—

$CH(CH_3)(CH_3)OH$ is the secondary alcohol *dimethyl carbinol* (propylic alcohol).
$CH(C_2H_5)(CH_3)OH$,, ,, *ethylmethyl carbinol* (butylic alcohol).

(*γ.*) If three units of hydrogen of the carbinol be replaced by three of the group (C_nH_{2n+1}), the alcohol is then called a *tertiary alcohol.* Thus—

$C(CH_3)(CH_3)(CH_3)OH$ is the tertiary alcohol *trimethyl carbinol* (butylic alcohol).
$C(C_2H_5)(CH_3)(CH_3)OH$,, ,, *ethyldimethyl carbinol* (amylic alcohol).

It will therefore be understood that an alcohol is regarded as primary, secondary, or tertiary, accordingly as the carbon atom in combination with the hydroxyl group, be directly combined with 1, 2, or 3 other carbon atoms. It will further be evident why no isomeric modifications of methylic or ethylic alcohol are possible.

The following list includes the principal *secondary alcohols*:—

NAME.	Formulæ.	Boiling point.	
		° F.	° C.
Dimethyl carbinol	$CH(CH_3)_2OH$	185	85·0
Ethyl methyl carbinol	$CH(CH_3)(C_2H_5)OH$	207	97·2
Methyl-isopropyl carbinol	$CH.CH(CH_3)_3OH$	226	107·8
Methyl propyl carbinol..	$CH(CH_3)(C_3H_7)OH$	248	120·0
Methyl butyl carbinol	$CH(CH_3)(C_4H_9)OH$	277	136·1
Methyl pentyl carbinol..	$CH(CH_3)(C_5H_{11})OH$	320	160·0
Methyl hexyl carbinol	$CH(CH_3)(C_6H_{13})OH$	358	181·1
Methyl nonyl carbinol	$CH(CH_3)(C_9H_{19})OH$	445	225·5

The following *tertiary alcohols* are known:—

Name.	Formulæ.	Boiling point.	
		° F.	° C.
Trimethyl carbinol	$C(CH_3)_3OH$	179	82
Dimethyl ethyl carbinol	$C(CH_3)_2(C_2H_5)OH$	212	100
Dimethyl isopropyl carbinol ..	$C(CH_3)_2(CH_3)_2CH.OH$	234	112
Dimethyl propyl carbinol	$C(CH_3)_2(C_3H_7)OH$	239	115
Methyl diethyl carbinol	$C(CH_3)(C_2H_5)_2OH$	248	120
Triethyl carbinol	$C(C_2H_5)_3OH$	284	140
Diethyl propyl carbinol	$C(C_2H_5)_2(C_3H_7)OH$	302	150

It will be convenient here to note the different effects of oxidizing agents on these three classes of alcohols :—

(*α*.) *Primary alcohols.*—These yield, by oxidation, three products; *viz.*, (1) an *aldehyde;* (2) a *monobasic acid;* and (3) an *ethereal salt*, the relative quantities of each of these products being dependent on many causes, such as the temperature, the alcohol, the oxidizing agent, and the quantity of water present. Thus :—

(1.) $$CH_3CH_2(OH) + O = CH_3COH + H_2O.$$
Ethylic alcohol + Oxygen = Acetic aldehyde + Water.

(2.) $$CH_3COH + O = CH_3COOH.$$
Acetic aldehyde + Oxygen = Acetic acid.

(3.) $$CH_3COOH + C_2H_5(OH) = CH_3COO(C_2H_5) + H_2O.$$
Acetic acid + Ethylic alcohol = Ethylic acetate + Water.

Thus a primary alcohol yields, on oxidation, an aldehyde, an acid containing the same number of carbon atoms as the alcohol oxidized, and an ethereal salt.

(*β*.) *Secondary alcohols.*—These yield *no aldehyde* on oxidation, but (1) a *ketone*, which, by the prolonged action of the oxidizing agent, becomes (2) *an acid*, but *which acid contains a less number of carbon atoms than the alcohol oxidized.*

(*γ*.) *Tertiary alcohols.*—These yield *no ketone*, and *no aldehyde* on oxidation, but *one or more acids of the acetic series.* Possibly a ketone may be formed, but it has never yet been discovered.

Preparation (*General Methods*) *of the Normal Primary Alcohols.*

(1.) *From the paraffins* (C_nH_{2n+2}).—This is illustrated in the preparation of methylic alcohol from methane (CH_4), as follows :—

(*α*.) A monochlorinated derivative of the paraffin is first formed, by the action of chlorine on the paraffin. Thus :—

$$CH_4 + Cl_2 = HCl + CH_3Cl.$$
Methane + Chlorine = Hydrochloric acid + Methyl chloride.

(*β*.) By the action of argentic acetate on this chlorinated derivative, an ethereal salt is formed. Thus, *e.g.* :—

$$CH_3Cl + AgC_2H_3O_2 = AgCl + CH_3(C_2H_3O_2).$$

Methyl chloride + Argentic acetate = Argentic chloride + Methylic acetate.

(γ.) By the action of potassic hydrate on this ethereal salt, potassic acetate and methylic alcohol are formed.

$$CH_3(C_2H_3O_2) + KHO = CH_3(OH) + KC_2H_3O_2.$$

Methylic acetate + Potassic hydrate = Methylic alcohol + Potassic acetate.

[Conversely it may be noted that the alcohol may be converted into its corresponding paraffin by first forming a chlorine derivative, and then acting on the chlorine derivative with nascent hydrogen (*see* page 626).]

(2.) *From the olefines* (C_nH_{2n}). — This may be effected by two methods, which may be illustrated in the formation of ethylic alcohol from ethylene (C_2H_4) :—

(A.) (*First process.*) (*a.*) The olefine is first acted on with sulphuric acid, whereby an acid ether of sulphuric acid is formed. Thus :—

$$C_2H_4 + H_2SO_4 = C_2H_5.HSO_4.$$

Ethylene + Sulphuric acid = (Sulpho-vinic acid) or hydric ethylic sulphate.

(*β.*) This ethereal salt is now distilled with water, when the alcohol and sulphuric acid are formed. Thus :—

$$C_2H_5.HSO_4 + H_2O = C_2H_5(HO) + H_2SO_4.$$

Sulpho-vinic acid + Water = Ethylic alcohol + Sulphuric acid.

(B.) (*Second process.*) (*a.*) By the action of hypochlorous acid on the olefine, a monochlorinated monohydric alcohol is formed. Thus :—

$$C_2H_4 + HClO = C_2H_4Cl(OH).$$

Ethylene + Hypochlorous acid = Chlorinated ethylic alcohol.

(*β.*) When this is acted on with nascent hydrogen, the alcohol and hydrochloric acid are formed :—

$$C_2H_4Cl(OH) + H_2 = C_2H_5(OH) + HCl.$$

Chlorinated ethylic alcohol + Hydrogen = Ethylic alcohol + Hydrochloric acid.

[Conversely, by the abstraction of the elements of water, the olefine may be prepared from the alcohol. Thus :—

$$C_2H_5(OH) - H_2O = C_2H_4.$$

Ethylic alcohol — Water = Ethylene.]

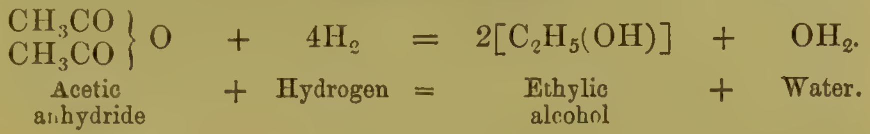
(3.) *From the normal primary* (*a*) *aldehydes*, or *from the* (*β*) *anhydrides of the acetic series.*—By the action of nascent hydrogen in each case :—

$$(a.)\ H(COH) + H_2 = CH_3(OH);\quad CH_3(COH) + H_2 = C_2H_5(OH).$$

Formic aldehyde + Hydrogen = Methylic alcohol; Acetic aldehyde + Hydrogen = Ethylic alcohol.

[By the action of nascent hydrogen on the isoprimary aldehydes of the acetic series, isoprimary alcohols are formed.]

(β.)



$$\left.\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\right\}O + 4H_2 = 2[C_2H_5(OH)] + OH_2.$$

Acetic anhydride + Hydrogen = Ethylic alcohol + Water.

(4.) One alcohol may be prepared *from the alcohol immediately preceding it in the series.*—Thus formic aldehyde yields methylic alcohol, and methylic alcohol may be made to yield ethylic alcohol. Thus :—

(α.) *Iodomethane* (CH_3I) is first formed by the action of hydriodic acid on methylic alcohol.

(β.) *Cyanomethane* ($CH_3(CN)$) is then formed by the action of potassic cyanide on iodomethane.

(γ.) *Sodic acetate* ($NaC_2H_3O_2$) is formed by digesting cyanomethane with sodic hydrate.

(δ.) *Acetic aldehyde* (CH_3COH) is formed by distilling sodic acetate with potassic formate.

(ε.) *Ethylic alcohol* ($C_2H_5(OH)$) is formed by the action of nascent hydrogen on acetic aldehyde.

Similarly normal primary propylic alcohol may be prepared from ethylic alcohol, etc.

Normal secondary alcohols are prepared (α) by the action of nascent hydrogen on the normal primary ketones, and (β) from the normal primary paraffins.

Tertiary alcohols may be prepared by the action of water on the product formed by the action of the zinc organo-metallic compounds on the acid chlorides of the formula $C_nH_{2n+1}COCl$.

General Properties.—(α.) *Physical.* All the alcohols of the ethylic series are colorless, and possess a more or less powerful odor. The first nine are colorless liquids. The first two (methylic and ethylic alcohol) are mobile liquids, and are soluble in water in all proportions, but the third (propylic alcohol) has not unlimited solubility. From this point the liquids get thicker, their boiling points higher, and their solubility in water less. Thus butylic alcohol is not very soluble, amylic alcohol is very sparingly soluble, and hexylic alcohol is insoluble in water. Caprylic alcohol leaves a greasy stain when dropped on paper. From nonylic alcohol downwards, the members of the series are solid.

(β.) *Chemical.* With *phosphorus pentasulphide*, the ethylic series form mercaptans or sulphydrates ($5(C_2H_5(OH)) + P_2S_5 = 5C_2H_5(SH)$ (*ethylic sulphydrate*) + P_2O_5); with *oxyacids* they form ethereal salts ($C_2H_5(OH) + HNO_3 = (C_2H_5)NO_3$ (*ethylic nitrate*) + H_2O); with *haloid acids* or with *compounds of phosphorus and the haloids*, they form monohaloid derivatives of the corresponding paraffins ($CH_3(OH) + HI = CH_3I$ (*iodomethane*) + H_2O); with the *alkaline metals*, hydrogen is evolved, and a metallic derivative formed ($2(C_2H_5(OH)) + Na_2 = 2(C_2H_5(ONa)) + H_2$), which metallic derivative is decomposed by water, with the formation of a metallic hydrate and the alcohol ($C_2H_5(ONa) + H_2O = C_2H_5(OH) + NaHO$). Their reactions *with oxidizing agents* have been described (p. 659), whilst *with dehydrating agents* the corresponding olefine is formed by the abstraction of water ($C_2H_5(OH) - H_2O = C_2H_4 + H_2O$).

(1.) **Methylic Alcohol.** (CH_3OH) or Me(OH). [*Molecular weight*, 32. *Molecular volume* ☐☐. *Specific gravity*, 0·798. *Boils at* 151·7° F. (66·5° C.) 100 c.i. *of the vapor weigh* 24·684 *grs., and* 1 *litre* 1·433 *grms.*]

Synonyms.—Carbinol; Wood or Pyroxylic spirit; Hydroxymethane; Pyroligneous ether.

Preparation.—1. From the paraffin methane (General Methods, 1).

2. From formic aldehyde (General Methods, 3 (*a*)).

3. By the action of potassic hydrate on the oil of the *Gaultheria procumbens* (wintergreen; methylic salicylate).

[This oil was the first vegetable product prepared artificially. Thus:—By the action of potassic hydrate on salicin, salicylic acid is formed, and this, when distilled with wood spirit and sulphuric acid yields the artificial oil.]

$$C_6H_4(OH).CO_2.CH_3 + KHO = C_6H_4(OH).CO_2K + CH_3(OH).$$

Methylic salicylate + Potassic hydrate = Potassic salicylate + Methylic alcohol.

4. By the action of heat on the nitrite of methylamine:—

(*α*.) Methylamine is formed by the action of nascent hydrogen on hydrocyanic acid; thus:—

$$HCN + 2H_2 = CH_3.H_2N.$$

Hydrocyanic acid + Hydrogen = Methylamine.

(*β*.) By boiling the solution of nitrite of methylamine, nitrogen, water, and methylic alcohol are formed; thus—

$$CH_3.H_3N(NO_2) = N_2 + H_2O + CH_3(OH).$$

Nitrite of methylamine = Nitrogen + Water + Methylic alcohol.

5. *Commercial process.* Prepared from the watery liquid, or *crude wood vinegar* as it is called, produced by the destructive distillation of wood (page 597).

This watery liquid is first of all distilled, the portion passing over at a temperature below 212° F. (100° C.) being collected separately. This contains methylic alcohol, acetone, acetate of methyl, and certain oily substances to which its odor is largely due. To this distillate slaked lime is added, and the clear liquor (that is, the liquid drawn from the centre, by which means the lime which sinks and the oil that floats are avoided) is several times redistilled. This distillate is now saturated with calcic chloride, whereby a crystalline compound ($CaCl_2,4CH_4O$), containing four molecules of methylic alcohol and one molecule of calcic chloride, is formed. This solid residue is now heated below 212° F. (100° C.) (beyond which temperature it would be decomposed), to drive off any acetone or methylic acetate present. Water is now added to the dried residue to decompose it, and the alcohol distilled off. Finally the methylic alcohol is purified by rectification, and rendered anhydrous by distillation after digestion with powdered quicklime.

The purest methylic alcohol is prepared by the action of water on methylic oxalate.

Properties.—(*a.*) *Physical.* When *pure,* methylic alcohol is a thin colorless liquid, having a taste and odor very like ethylic alcohol. The *crude alcohol* has an offensive odor and a burning taste. Specific gravity 0·798 at 20° C. Boiling point 151·7° F. (66·5° C.). It mixes with water (condensation resulting) in all proportions, and it is (like ethylic alcohol) a solvent of resins, volatile oils, etc.

(*β.*) *Chemical. It unites with certain salts* in the capacity of water of crystallization (*e.g.* $CaCl_2.2CH_3.OH$). It unites *with the alkaline metals,* forming methylates, hydrogen being evolved ($2CH_3.OH + K_2 = 2CH_3.OK + H_2$). It also dissolves caustic soda, potash, baryta, etc. ($BaO,2CH_4O$). *Distilled with chloride of lime and water* it forms chloroform (*see* Chloroform). By *oxidation*, as by exposure to air on platinum black, it yields formic acid ($CH_3(HO) + O_2 = H_2O + CH_2O_2$).

It burns with a pale-colored flame, which deposits no soot.

Uses.—In the arts it is employed as a solvent of resins for varnishes, in the preparation of aniline colours, and for burning in lamps as a *heating* power only, for mixing with pure alcohol to form *methylated spirit* (= ethylic alcohol 90 parts—methylic alcohol 10 parts. Specific gravity 0·83), etc.

(2.) **Ethylic Alcohol** ($C_2H_5(OH)$ or Et (OH). [*Molecular weight,* 46. *Molecular volume* □□. *Specific gravity,* 0·7938 at 15° C. *Boiling point,* 173° F. (78·4° C.).]

Synonyms.—Alcohol; Vinic alcohol; Spirits of wine; Methyl carbinol, $CH_3(CH_2OH)$; *Hydroxyl ethene.*

Preparation.—(1.) From the olefine ethylene, C_2H_4 (*see* General Methods, 2).

[Note. Ethylene may be prepared by the direct union of carbon and hydrogen.]

(2.) By the fermentation of grape sugar.

Properties.—A colorless liquid having an agreeable taste and odor. It burns with a non-luminous smokeless flame, requiring three times its own volume of oxygen for complete combustion. When imperfectly burnt, an acrid volatile compound is formed. Anhydrous alcohol boils at 173° F. (78·3° C.) at standard pressure. By dilution the boiling point becomes gradually higher.

Action of Water on Alcohol.—Alcohol is very hygroscopic and mixes with water in all proportions, heat and contraction of volume resulting from their admixture.

To determine the amount of alcohol present in any mixture, a given quantity must be distilled until all the alcohol has passed over. The distillate is then to be weighed, and its specific gravity taken, the percentage of alcohol being determined by table (Table VII.).

Proof spirit (that is the weakest spirit that will fire gunpowder when moistened with it and ignited), has a gravity of 0·92 and contains in every 100 parts by weight—

Water	50·76
Alcohol	49·24.

A weaker spirit does not fire gunpowder, and is termed "*under proof*," a stronger spirit being spoken of as "*over proof.*"

By distillation a weak spirit may be made to yield a 90 per cent. alcohol (that is, a spirit containing 90 per cent. of alcohol), but distillation will not effect the separation of the last 10 per cent. of water. A further separation of 5 per cent. of water (that is, the formation of a 95 per cent. alcohol) may be effected by enclosing the alcohol in a bladder, through which the water exudes more rapidly than the alcohol. An alcohol of 89 per cent. may be obtained by dissolving dry potassic carbonate in the alcohol to saturation. The solution separates into two layers, the upper consisting of spirit of 89 per cent., and the lower of water, containing potassic carbonate in solution. Absolute alcohol (100 per cent.) is prepared by digesting the alcohol with quicklime for three or four days, and distilling. It is very hygroscopic.

Commercial rectified spirit	contains	13 or 14	per cent	of water.	Sp. gr. 0·835.
,,	proof	,,	49·5	,,	,,	Sp. gr. 0·9198.

Alcohol dissolves numerous salts, but no salts are soluble in alcohol that are insoluble in water. It dissolves most deliquescent salts, and but few efflorescent salts. With some it forms definite crystalline compounds, called alcoholates, *i.e.*, salts containing alcohol in the place of water of crystallization, as, *e.g.*, $ZnCl_2,2C_2H_6O$, etc. These bodies are decomposed by water. It also dissolves the *alkaline metals*, hydrogen being evolved, forming C_2H_5KO and C_2H_5NaO; also the elementary gases O, H, and N; also the gaseous hydrocarbons; also certain organic bodies, such as the alkaloids, resins, essential oils, etc.

When the vapor of alcohol is passed through a red-hot tube, it yields marsh gas, carbonic oxide and hydrogen ($C_2H_6O = CH_4 + H_2 + CO$), other bodies, such as C_2H_6, C_6H_6, etc., being also formed.

Action of Chlorine.—By the action of chlorine on *absolute alcohol*, continued until hydrochloric acid ceases to be evolved, ethylic acetate and chloral hydrate (trichloraldehyde) are formed:—

$$2C_2H_5.OH + 4Cl_2 = CCl_3.CH(OH)_2 + C_2H_5Cl + 4HCl.$$

Ethylic alcohol + Chlorine = Chloral hydrate + Ethylic chloride + Hydrochloric acid.

By the action of chlorine on *dilute alcohol*, aldehyde is formed but no chloral.

By the action of chlorine on alcohol *in the presence of alkalies* (or by the action on the alcohol of chloride of lime), chloroform and carbonic anhydride are formed. Thus:—

$$C_2H_5(OH) + 5Cl_2 + H_2O = CO_2 + 7HCl + CHCl_3.$$

Ethylic alcohol + Chlorine + Water = Carbonic anhydride + Hydrochloric acid + Chloroform.

Numerous intermediate products may also be formed.

By *oxidation* alcohol (C_2H_6O) is converted into aldehyde (C_2H_4O), and finally, into acetic acid ($C_2H_4O_2$).

Sulphuric acid combines with dilute alcohol to form ethyl-sulphuric acid $(C_2H_5)HSO_4$. When sulphuric anhydride acts on anhydrous alcohol, a white substance called ethionic oxide is formed ($C_2H_4S_2O_6$), which, when dissolved in water, forms ethionic acid ($C_2H_6S_2O_7$).

When alcohol is allowed to act on fused potassic hydrate, hydrogen is evolved and potassic acetate is formed. Thus:—

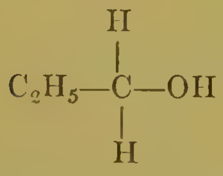
$$KHO + C_2H_5(OH) = KC_2H_3O_2 + 2H_2.$$

Potassic hydrate + Alcohol = Potassic acetate + Hydrogen.

(3.) **Propylic Alcohol,** $C_3H_7(OH)$.—This alcohol exists in two isomeric modifications, viz., *a normal primary propylic alcohol*, termed *ethyl carbinol*, and a *secondary isopropylic alcohol*, called *dimethyl carbinol*. These may be figured as follows:—

(α.) Normal propylic alcohol (primary).

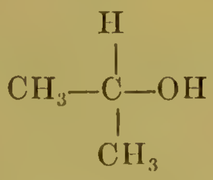
$=C_2H_5.CH_2.OH$



$$C_2H_5-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH$$

(β.) Isopropylic alcohol (secondary).

$=CH(CH_3)_2OH$



$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-OH$$

(α.) *Normal propylic alcohol,* or ethyl carbinol may be prepared from ethyl alcohol (*see* General Methods, 4, page 561).

Properties.—An oily liquid, yielding propionic acid by oxidation.

(β.) *Isopropylic alcohol,* or dimethyl carbinol may be prepared from acetone $(CH_3)_2CO''$ by the action upon it of nascent hydrogen. Thus:—

$$(CH_3)_2CO \quad + \quad H_2 \quad = \quad CH(CH_3)_2(OH).$$

Acetone + Hydrogen = Isopropylic alcohol.

Properties.—A colorless liquid; sp. gr. 0·791° F. at 15° C. Boils at 185° F. (85° C.). It does not freeze at —4° F. (—20° C.). It has no action on a polarized ray of light. It forms hydrates of remarkable stability. It yields, by oxidation, first (*α*), acetone; and finally (*β*), acetic acid.

$$(\alpha.)\ CH(CH_3)_2(OH) \quad + \quad O \quad = \quad CO(CH_3)_2 \quad + \quad H_2O.$$

Isopropylic alcohol + Oxygen = Acetone + Water.

$$(\beta.)\ CO(CH_3)_2 \quad + \quad 2O_2 \quad = \quad CH_3CO_2H \quad + \quad CO_2 \quad + \quad H_2O.$$

Acetone + Oxygen = Acetic acid + Carbonic anhydride + Water.

(4.) **Butylic Alcohol,** $C_4H_9(OH)$.—There are four isomeric modifications of this alcohol. Thus—

(*α*.) $CH_3.CH_2.CH_2.CH_2(OH)$, *propyl carbinol,* or *normal primary butylic alcohol,* may be prepared from butylic aldehyde by the action of nascent hydrogen. It boils at 240·8° F. (116° C.).

On oxidation it yields *normal butyric acid*—

$$C_4H_9(OH) \quad + \quad O_2 \quad = \quad C_3H_7CO(OH) \quad + \quad H_2O.$$

Butylic alcohol + Oxygen = Normal butyric acid + Water.

(*β*.) $CH(CH_3)_2CH_2(OH)$, *isopropyl carbinol,* or *iso-primary butylic alcohol,* is found in the fusel oil formed when beet sugar molasses is fermented. It boils at 228·2° F. (109° C.).

On oxidation it yields *iso-butyric acid*—

$$C_4H_9(OH) \quad + \quad O_2 \quad = \quad CH(CH_3)_2CO(OH).$$

Butylic alcohol + Oxygen = Isobutyric acid.

(*γ*.) $C(CH_3)(C_2H_5)H(OH)$. *Methyl ethyl carbinol,* or *secondary butylic alcohol,* is prepared by the action of moist argentic oxide on methyl-ethyl-iodo-methane, formed by distilling *erythrite* ($C_4H_6(OH)_4$), a saccharine substance, with fuming hydriodic acid. Thus—

$$C(CH_3)(C_2H_5)HI \quad + \quad AgHO \quad = \quad AgI \quad + C(CH_3)(C_2H_5)H(OH).$$

Methyl-ethyl-iodo-methane + Argentic hydrate = Argentic iodide + Secondary butylic alcohol.

It is a colorless oily liquid, having a sp. gr. of 0·85° at 32° F. (0° C.).

On oxidation it yields, first, *methylethylketone,* and finally, *acetic acid.*

(*δ*.) $C(CH_3)_3OH$.—*Trimethylcarbinol,* or *tertiary butylic alcohol,* is prepared by the action of water on the product formed by the action of acetic chloride on zinc methide. It boils at 180·5° F. (82·5° C.).

On oxidation it yields isobutyric, acetic and formic acids; also acetone, isobutylene, carbonic anhydride, and water.

(5.) **Amylic Alcohol** ($C_5H_{11}(OH)$).—There may be as many as eight isomeric modifications of this alcohol, five of which are known.

The ordinary amylic alcohol, or iso-amylic alcohol (isobutyl carbinol), is the fusel oil of the distiller. It is said to be a mixture of two different alcohols, one rotating a ray of polarized light to the left, and boiling at 262·4° F. (128° C.), the other without polar action, and boiling at 266° F. (130° C.). Amylic alcohol is an oily liquid, having a sp. gr. 0·8111. It imparts a transient greasy stain to paper.

On oxidation both the varieties named above, yield valeric acid :—

$$\begin{array}{ccccccc} C_4H_9(CH_2)OH & + & O_2 & = & C_4H_9.CO(OH) & + & H_2O. \\ \text{Amylic alcohol} & + & \text{Oxygen} & = & \text{Valeric acid} & + & \text{Water.} \end{array}$$

Vinylic Series.

SERIES II.—*Formula* $C_nH_{2n-1}OH$.

The relationship between the vinylic series and the olefines, is identical to that subsisting between the ethylic series of alcohols and the paraffins. Thus :—

(*a.*) *Paraffin ; Methane* CH_4 and $CH_3(OH)$, *methylic alcohol.*

(*β.*) *Olefine ; Ethylene* C_2H_4 and $C_2H_3(OH)$, *vinylic alcohol.*

This series includes—

1. Vinylic alcohol	$C_2H_3(OH)$
2. Allylic alcohol	$C_3H_5(OH)$

(1.) **Vinylic Alcohol** ($C_2H_3(OH)$). It is prepared (*a*) by first combining acetylene with sulphuric acid, and (*β*) afterwards distilling the product with water :—

$$\begin{array}{cccccc} (a.) & C_2H_2 & + & H_2SO_4 & = & (C_2H_3)HSO_4. \\ & \text{Acetylene} & + & \text{Sulphuric acid} & = & \text{Sulphovinylic acid.} \end{array}$$

$$\begin{array}{cccccccc} (\beta.) & (C_2H_3)HSO_4 & + & H_2O & = & H_2SO_4 & + & C_2H_3(OH). \\ & \text{Sulphovinylic acid} & + & \text{Water} & = & \text{Sulphuric acid} & + & \text{Vinylic alcohol.} \end{array}$$

It is a pungent liquid, isomeric with aldehyde and ethylenic oxide.

(2.) **Allylic Alcohol** ($C_2H_5(OH)$). [*Specific gravity at* 32° F. (0° C.) 0·8709. *Boiling point,* 204·8° F. (96° C.).]

Preparation.—It may be formed from glycerin, as follows :—

(1.) (*a.*) *Allylic iodide* (C_3H_5I) is first formed by the action of phosphorus iodide on glycerin—

$$\begin{array}{ccccccccc} 2(C_3H_5(OH)_3) & + & P_2I_4 & = & 2C_3H_5I & + & 2H_3PO_3 & + & I_2. \\ \text{Glycerine} & + & \text{Phosphorus iodide} & = & \text{Allylic iodide} & + & \text{Phosphorous acid} & + & \text{Iodine.} \end{array}$$

(*β.*) *Allylic oxalate* is then formed by the action of argentic oxalate on allylic iodide—

$$2C_3H_5I + Ag_2C_2O_4 = 2AgI + (C_3H_5)_2C_2O_4.$$

Allylic iodide + Argentic oxalate = Argentic iodide + Allylic oxalate.

(γ.) *Allylic alcohol* (+oxamide) is then formed by the action of ammonia on the allylic oxalate—

$$(C_3H_5)_2C_2O_4 + 2NH_3 = 2(C_3H_5(OH)) + N_2(C_2O_2)''H_4.$$

Allylic oxalate + Ammonia = Allylic alcohol + Oxamide.

(2.) By the action of heat on a mixture of glycerin and oxalic acid:—

$$C_3H_5(OH)_3 + C_2H_2O_4 = 2H_2O + 2CO_2 + C_3H_5(OH).$$

Glycerine + Oxalic acid = Water + Carbonic anhydride + Allyilc alcohol.

Properties.—A colorless liquid. Sp. gr. 0·8709. Boils at 204·8° F. (96° C.). It is combustible and soluble in water in all proportions.

Its reactions resemble those of ethylic alcohol.

With *the haloids* it forms both derivatives, such as C_3H_5Br, etc., and compounds such as $C_3H_5Cl_2(OH)$. With *sulphuric acid* it forms allylic sulphuric acid, $(C_3H_5)HSO_4$. With the *alkaline metals* it forms substitution products. *Nascent hydrogen* has no action upon it. By *oxidation* it yields acrolein, formic acid and carbonic anhydride.

The *allylic sulphide* constitutes the oil of garlic $[(C_3H_5)_2S]$, and is formed by acting on allylic iodide with potassic sulphide (*α*). Oil of mustard contains *allylic sulphocyanate,* and is formed artificially by the action of potassic sulphocyanate on allylic iodide (*β*).

(*α*.) $2C_3H_5I + K_2S = 2KI + (C_3H_5)_2S.$

Allylic iodide + Potassic sulphide = Potassic iodide + Allylic sulphide (garlic oil).

(*β*.) $C_3H_5I + KNCS = KI + (C_3H_5)(NCS).$

Allylic iodide + Potassic sulphocyanate = Potassic iodide + Allylic sulphocyanate (mustard oil).

SERIES III.—*Formula* $C_nH_{2n-3}(OH)$.

This includes—

Propargylic Alcohol $(C_3H_3(OH))$. [*Specific gravity,* 0·9628 *at* 68° F. (20° C.). *Boils at* 239° F. (115° C.).]

Preparation.—By the action of potassic hydrate on mono-bromallylic alcohol—

$$C_3H_4Br(OH) + KHO = C_3H_3(OH) + KBr + H_2O.$$

Monobromallylic alcohol + Potassic hydrate = Propargylic alcohol + Potassic bromide + Water.

Properties.—A colorless mobile liquid.

Benzylic Series—The Phenols.

SERIES V.—*Formula* $C_nH_{2n-7}(OH)$.

These alcohols may be divided into two classes:—

. Benzylic Series (normal alcohols).			Boiling point.		Melts at	
Alcohols.	Formulæ.	Specific Gravity.	° F.	° C.	° F.	° C.
Benzylic	$C_7H_7(OH)$	1·051 at 14° C.	403·7	206·5		
Xylilic (toluylic) .	$C_8H_9(OH)$		422·6	217·0	139·1	59·5
Cumilic	$C_{10}H_{13}(OH)$		469·4	243·0		
Sycocerylic	$C_{18}H_{29}(OH)$				194·0	90·0
II. Phenols.						
Phenylic	$C_6H_5(OH)$	1·068	356	180	95·0	35·0
Cresylic	$C_6(CH_3)H_4(OH)$		383—392	195—200		
Phlorol	$C_6(C_2H_5)H_4(OH)$	1·037 at 12° C.	374—392	190—200		
Dimethyl phenylic (xylenol)	$C_6(CH_3)_2H_3(OH)$		410	210		
Thymylic	$C_6(C_2H_5)_2H_3(OH)$		428	220	111·2	44·0

These alcohols are derivatives of the C_nH_{2n-6} series of hydrocarbons, by the substitution of a semi-molecule of hydroxyl for one atom of hydrogen.

They form well-marked substitution compounds when acted on by chlorine, nitric acid, etc., but they never form additive compounds; for like the hydrocarbons, from which they are derived, they are fully saturated bodies.

The haloid acids are without action on them, whilst with sulphuric acid they yield sulphonic acids, which, by fusion with potassic hydrate, are convertible into dihydric alcohols.

It will be noted that all the series of alcohols preceding the phenols differ strikingly in these respects from the phenols. (α.) They neither form substitution compounds under the same circumstances, nor with the same ease, as the phenols. (β.) With the haloid acids the preceding series form derivatives, and (γ) with sulphuric acid, acid ethereal salts, which, when treated with water, reproduce sulphuric acid and the alcohol.

Lastly, the products of the oxidation of the phenols and of the alcohols of the preceding series, are completely different.

Preparation.—(1.) *From the benzenes* (C_nH_{2n-6}). The conversion may be effected in one of two ways:—

(A.) By first acting on the hydrocarbon with sulphuric acid, and afterwards fusing the potassic salt of the monosulphonic acid formed, with potassic hydrate.

(B.) By the action of nitrous acid on the amido-derivative of the hydrocarbon.

Benzylic Alcohol (C_7H_7OH or $C_6H_5(CH_2)OH$). [*Specific gravity,* 1·051 *at* 14° C. *Boils at* 206·5° C.]

Preparation.—(1.) By the action of alcoholic potassic hydrate on benzoic aldehyde (oil of bitter almonds)—

$$2C_6H_5COH + KHO = C_7H_7(OH) + K(C_7H_5O)O.$$

Benzoic aldehyde + Potassic hydrate = Benzylic alcohol + Potassic benzoate.

(2.) *From toluene.* By the action of potassic hydrate on toluylic chloride:—

$$C_7H_7Cl + KHO = C_7H_7(OH) + KCl.$$

Toluylic chloride + Potassic hydrate = Benzylic alcohol + Potassic chloride.

(3.) By the action of nascent hydrogen on benzoic or hippuric acids.

Properties.—A colorless, oily, highly refracting liquid, insoluble in water, but soluble in all proportions in alcohol, ether, acetic acid, and carbon disulphide. With *hydrochloric acid* it forms benzylic chloride, $C_6H_5.CH_2.Cl$. With *strong sulphuric acid* it forms a resinous body. Distilled with sulphuric and acetic acids, it forms benzyl acetate ($C_7H_7(OC_2H_3O)$). By *oxidation with dilute nitric acid* it forms benzoic aldehyde (C_6H_5COH), and with *chromic acid* benzoic acid, ($C_6H_5CO_2H$).

Phenylic Alcohol ($C_6H_5(OH)$).—[*Molecular weight,* 94. *Molecular volume* ☐. *Specific gravity,* 1·065 *at* 64·4° F. (18° C.). *Fuses at* 93·2° F. (34° C.). *Boils at* 370·4° F. (188° C.). 100 c.i. *of vapor weigh* 32·945 grms., *and* 1 litre 4·211 grms.]

Synonyms.—Carbolic acid; Phenylic acid; Phenic acid; Oxy-benzene; Phenol; Coal-tar Kreasote.

Natural History.—It is found in the urine of cows and other animals.

Preparation.—(1.) By the action of nitrous acid on amidobenzene (aniline). Thus:—

$$C_6H_5(NH_2) + HNO_2 = C_6H_5(OH) + H_2O + N_2.$$

Aniline + Nitrous acid = Phenylic alcohol + Water + Nitrogen.

(2.) By distilling salicylic acid either alone or mixed with lime, etc.

$$C_7H_6O_3 = C_6H_5(OH) + CO_2.$$

Salicylic acid = Phenylic alcohol + Carbonic anhydride.

(3.) (*Commercial preparation.*) The dead oil of coal-tar is first distilled, that portion which passes over between 300° and 400° F. (149° and 205° C.) being collected separately. This is shaken up with a hot concentrated solution of sodic hydrate, which dissolves the carbolic acid, and enables it to be separated from the oil that floats on the surface. The alkaline solution is then decomposed with hydrochloric acid, when the carbolic acid separates as an oily layer on the surface.

This is drawn off, digested with calcic chloride to remove the water, and distilled. By exposing the distilled acid to a low temperature it solidifies. The crystals are collected, drained, and again distilled.

Sometimes the dead oil (without distillation) is treated with a mixture of slaked lime and water, and the solution which contains the carbolic acid, drawn off from the oil which swims on the surface.

Tests for the purity of carbolic acid—

(1.) Shake up half a dram of the acid with half a pint of warm water. The acid is perfectly soluble in the water, whilst any dead oil present as an impurity in the acid will float on the surface.

(2.) Five parts of pure carbolic acid are soluble in a mixture of one part of caustic soda and ten parts of water.

(3.) Expose a mixture of carbolic acid (3 parts by weight) and water (1 part) to the cold of ice, when crystals are deposited having the formula $2C_6H_6O.H_2O$ soluble in alcohol, in ether, and in water. The crystals melt at 61° F. (16·1° C.).

To *distinguish carbolic acid from kreasote* (the product of wood)—

CARBOLIC ACID.	KREASOTE.
1. Boils at 370° F. (187·8° C.).	1. Dries up at 212° F. (100° C.).
2. Does not affect a polarized ray.	2. Rotates a polarized ray to the right.
3. Is solidified by cooling.	3. Not solidified by ice and salt.
4. Forms a jelly when shaken with collodion.	4. Is unaffected by collodion.
5. Is soluble in a strong solution of ammonia or potassic hydrate.	5. Is insoluble in ammonia or in potassic hydrate solutions.
6. Solubility in water; 1 in 20 at 212° F.; 1 in 80 at 60° F.	6. Solubility in water; 1 in 130 at 60° F.
7. Ferric chloride turns the aqueous solution blue.	7. Solution not colored blue by ferric chloride.
8. Ferric chloride turns the solution in alcohol brown.	8. Ferric chloride turns the solution in alcohol green.

Properties.—(*a.*) *Physical.* Carbolic acid when pure, crystallizes in colorless needles which are very deliquescent, and melts at 93·2° F. (34° C.), forming an oily liquid, which boils at 370·4° F. (188° C.). It has a specific gravity at 18° C. of 1·065. Its odor is peculiar, and its action caustic. It is not easily decomposed even by a red heat. Distilled over heated zinc dust, it yields benzene. It is slightly soluble in water, but is very soluble in alcohol and in ether, and is a solvent of sulphur, iodine, etc. Its special action is antiseptic.

In appearance it closely resembles kreasote, from which it may be known by the tests already described.

(*β.*) *Chemical.*—Its solution is not acid to litmus. *The haloid elements* form with it substitution compounds (as $C_6H_3Cl_2(OH)$ and $C_6Cl_5(OH)$ *pentachlorophenol*). With *nitric acid* it forms $C_6H_4(NO_2)OH$, $C_6H_3(NO_2)_2OH$, and finally the substitution product $C_6H_2(NO_2)_3(OH)$, or *picric acid.* All its nitro-derivatives decompose the metallic carbonates. With *sulphuric acid* it forms phenol disulphonic acid, $C_6H_3OH(SO_3H)_2$. The *haloid acids* are without action upon it. The *alkalies* (but not the alkaline carbonates) dissolve it, forming phenates. By *oxidation* with chromic acid it yields phenoquinone.

$$\underset{\text{Phenylic alcohol}}{3[C_6H_5(OH)]} + O_3 + H_2O = \underset{\text{Pheno-quinone.}}{C_6H_4(O.OC_6H_5)_2} + 3H_2O.$$

Cresylic Alcohol (*Cresol*) $C_6H_4(CH_3)OH$.—This occurs in three modifications, which yield three isomeric cresol-sulphonic acids.

(α.) *Paracresol* is a solid crystalline body, boiling at 392° F. (200° C.). When fused with potassic hydrate, paracresol yields *potassic paroxybenzoate*, $C_6H_4(OH)CO_2K$.

(β.) *Metacresol* is a liquid, and boils at 392° F. (200° C.). When fused with potassic hydrate, metacresol yields *potassic metoxybenzoate.*

(γ.) *Orthocresol* is a liquid, and boils at 372·2° F. (189° C.). When fused with potassic hydrate, orthocresol yields *potassic salicylate* (orthoxybenzoate).

Thymylic Alcohol $C_6(C_2H_5)_2H_3(OH)$.—The thymols exist in two isomeric forms. *Thymol* (α) is found in the oil of thyme and other plants. It is a crystalline solid, melting at 111·2° F. (44° C), and boiling at 428° F. (220° C.). By the action of sulphuric acid it is completely converted into a sulpho-acid. *Thymol* (β) is a yellow viscid oil which, by the action of sulphuric acid, is only very partially converted into a sulpho-acid.

SERIES VI.—*Formula* $C_nH_{2n-9}(OH)$.

This includes—

Cinnamic alcohol.	$C_9H_9(OH)$	*Preparation.*—By heating styracin with potassic hydrate. With *nascent hydrogen* it forms phenylpropylic alcohol and allyl benzene. By *oxidation* it yields cinnamic aldehyde. Melting point, 91·4° F.; 33° C.
Cholesterin..	$C_{26}H_{43}(OH)$	A crystalline solid, present in different parts of the animal. It forms, by oxidation with chromic acid, oxycholic acid, $C_{26}H_{40}O_6$.

B.—DIHYDRIC ALCOHOLS.

The Glycols.

SERIES I.—*Formula* $C_nH_{2n}(OH)_2$.

This series includes—

GLYCOLS.	Formulæ.	Boiling Point.	
		° F.	° C.
Ethylene glycol	$C_2H_4(OH)_2$	387·5	197·5
Propylene ,,	$C_3H_6(OH)_2$	370·4—372·2	188—189
Butylene ,,	$C_4H_8(OH)_2$	361·4—363·2	183—184
Amylene ,,	$C_5H_{10}(OH)_2$	350·6	177
Hexylene ,,	$C_6H_{12}(OH)_2$	404·6	207
Octylene ,,	$C_8H_{16}(OH)_2$	455—464	235—240

The glycols (or diatomic alcohols) may be regarded (1) *as derivatives of the paraffins*, where two atoms of hydrogen are replaced by two semi-molecules of hydroxyl (OH). Thus—

Ethane C_2H_6 forms $C_2H_4(OH)_2$, *glycol.*
Propane C_3H_8 ,, $C_3H_6(OH)_2$, *propylene glycol*, etc.

Or (2) they may be regarded as *compounds of the olefines* with hydroxyl. Thus—

Ethylene C_2H_4 + $(OH)_2$ forms $C_2H_4(OH)_2$, *ethylene glycol.*
Propylene C_3H_6 + $(OH)_2$,, $C_3H_6(OH)_2$, *propylene glycol*, etc.

Preparation.—From the olefines. We may illustrate this in the preparation of glycol:—

(*a.*) A *dibromide* ($C_2H_4Br_2$) is first formed by the action of bromine on ethylene:—

(*β.*) A *diacetate of the olefine* is now formed, by the action of argentic or potassic acetate on the dibromide. Thus:—

$C_2H_4Br_2$	+	$2AgC_2H_3O_2$	=	$2AgBr$	+	$C_2H_4(C_2H_3O_2)_2$.
Ethylene dibromide	+	Argentic acetate	=	Argentic bromide	+	Ethylenic diacetate.

(*γ.*) A *glycol* (+potassic acetate) is now formed, by treating the diacetate with potassic hydrate. Thus:—

$C_2H_4(C_2H_3O_2)_2$	+	$2KHO$	=	$2KC_2H_3O_2$	+	$C_2H_4(OH)_2$.
Ethylenic diacetate	+	Potassic hydrate	=	Potassic acetate	+	Glycol.

Properties.—(*a.*) *Physical.* Ethylene glycol (commonly called *glycol*) is the only member of the series that has been particularly studied. The glycols are colorless liquids, without odor, freely soluble in water and in alcohol, and also (excepting ethylene glycol) in ether.

(*β.*) *Chemical.* The reactions of the glycols are similar to those of the monatomic alcohols, excepting in this, that having two semi-molecules of replaceable hydroxyl, two series of products result.

With sodium and potassium the glycols form two substitution products. Thus:—

$C_2H_4(HO)(NaO)$;	$C_2H_4(NaO)_2$.
Monosodic glycol;	Disodic glycol.

These compounds form the alcoholic ethers of the glycols when treated with a monatomic alcoholic iodide. Thus:—

$C_2H_4(OH)(ONa)$	+	C_2H_5I	=	NaI	+	$C_2H_4(C_2H_5O)(OH)$.
Monosodic glycol	+	Ethylic iodide	=	Sodic iodide	+	Ethylic ethynate.

Oxygen acids form with the glycols, ethereal salts, which are mono- or di-acid, according to the proportions of the reagents respectively used. The *haloid acids* and haloid phosphorus compounds form with them mono- and di-haloid derivatives. *Potassic hydrate*, when heated with glycol, forms potassic oxalate ($C_2H_4(OH)_2+2KHO=C_2O_2(OK)_2$

$+ 4H_2$). By *oxidation* glycol yields (α) first glycolic acid (other acids, varying with the glycol acted upon, being formed), and finally (β) oxalic acid.

(α.) $C_2H_4(OH)_2 + O_2 = CH_2(OH)CO(OH) + OH_2$.
Glycol + Oxygen = Glycollic acid + Water.

(β.) $CH_2(OH)CO(OH) + O_2 = C_2O_2(OH)_2 + H_2O$.
Glycollic acid + Oxygen = Oxalic acid + Water.

We may here note that the relationship between ethylic alcohol, ethylic aldehyde, and acetic acid, finds its counterpart in that subsisting between glycol, glyoxal (glycolic aldehyde), and oxalic acid. Thus:—

$CH_3.CH_2(OH)$, Ethylic alcohol,	CH_3COH, Aldehyde,	$CH_3.CO(OH)$; Acetic acid;
$CH_2(OH).CH_2(OH)$, Glycol,	$COH.COH$, Glyoxal,	$CO(OH)CO(OH)$. Oxalic acid.

Between glycol and ethylic alcohol, however, this point of difference is to be noted,—that whereas *ethylic alcohol* forms only *one* substitution compound severally with sodium, with sulphuric acid, etc., *glycol* forms *two*. Thus:—

Alcohol forms—	*Glycol forms*—
$C_2H_5(ONa)$,	$C_2H_4(OH)(ONa)$ and $C_2H_4(ONa)_2$,
$C_2H_5(HSO_4)$;	$C_2H_4(OH)(HSO_4)$ and $C_2H_4(HSO_4)_2$.

By heating glycol with ethylenic oxide in sealed tubes, a series of compounds, called *polyethylenic glycols* (or *alcohols*), are formed. They are the result of progressive condensation (although normal condensation to two volumes) with elimination of the elements of water. They are syrupy liquids. Diethylenic glycol boils at 473° F. (245° C.), each succeeding term of the series boiling at about 81 degrees Fahrenheit (45° C.) higher than the one below it. The following compounds are known:—

Alcohols.	Formulæ.
Diethylenic glycol	$C_4H_{10}O_3 = 2C_2H_4(OH)_2 - H_2O$
Triethylenic glycol	$C_6H_{14}O_4 = 3C_2H_4(OH)_2 - 2H_2O$
Tetrethylenic glycol	$C_8H_{18}O_5 = 4C_2H_4(OH)_2 - 3H_2O$
Pentethylenic glycol	$C_{10}H_{22}O_6 = 5C_2H_4(OH)_2 - 4H_2O$
Hexethylenic glycol	$C_{12}H_{26}O_7 = 6C_2H_4(OH)_2 - 5H_2O$

Orcins—Aromatic Glycols—Saligenin Series.

SERIES II.—*Formula* $C_nH_{2n-8}(OH)_2$.

This series, the members of which are derivatives of benzene, include—

Alcohols.	Formulæ.	Melting Pt.		Preparation, Properties, etc.
		° F.	° C.	
ydroquinone..	$C_6H_4(OH)_2$	351·5	177·5	*Preparation.*—By the dry distillation of quinic acid. By oxidation forms quinone.
esorcin	$C_6H_4(OH)_2$	210·2	99·0	*Preparation.*—By fusing the resin of galbanum or benzene disulphonic acid with potassic hydrate. Soluble in water, alcohol, and ether. Aqueous solutions give a violet with Fe_2Cl_6, and reduce $AgNO_3$. Forms substitution compounds.
yrocatechin .. (oxyphenol)	$C_6H_4(OH)_2$	232·7	111·5	*Preparation.*—By the distillation of catechin, etc., and by the action of alkalies on meta-iodophenol. With Fe_2Cl_6 gives a dark green color, and with plumbic acetate a white precipitate.
rcin	$C_6H_3,CH_3(OH)_2$	186·8	86·0	Found in the lichens used in the preparation of cudbear, litmus, etc. May be formed artificially. By the action of ammonia and free oxygen, forms *orcein* ($C_7H_7NO_3$?), the coloring matter of archil and cudbear. Forms numerous substitution products with the haloids and with nitric acid.
alicylic alcohol (saligenin)	$C_6H_4(OH)CH_2(OH)$	179·6	82·0	*Preparation.*—By the decomposition of salicin under the influence of a ferment (as synaptase), or of dilute sulphuric acid. By oxidation yields *salicylic aldehyde*, $C_6H_4(OH)COH$. With ferric salts, its aqueous solution gives an indigo blue coloration.

C.—TRIHYDRIC ALCOHOLS.

Trihydric alcohols are derived from saturated hydrocarbons by the substitution of three atoms of hydroxyl for three atoms of hydrogen. They are, therefore, compounds of trivalent alcohol radicals with three atoms of hydroxyl.

Glycerin Series.—SERIES I.—*Formula* $C_nH_{2n-1}(OH)_3$.

This includes—

Glycerin	$C_3H_5(OH)_3$ [derived from C_3H_8].
Amylglycerin ...	$C_4H_7(OH)_3$ [derived from C_4H_{10}].

Glycerin.—($C_3H_5(OH)_3 = C(CH_2.OH)_2H.OH.$) [*Specific gravity at* 60° F. (15·5° C.), 1·27. *Boils at* 355·1° F. (179·5° C.)].

Synonym.—Propenyl alcohol (*glycerol*).

Natural History.—Glycerin occurs in most animal and vegetable fats in combination with (that is, as glycerides or ethereal salts of) the acids of the acetic and oleic series. Olive oil, for example, contains *olein*, or a *glyceride of oleic acid;* suet contains *stearin*, or a *glyceride of stearic acid*; palm oil contains *palmitin*, or a *glyceride of palmitic acid.* Glycerin is usually prepared from these bodies as a bye-product during the manufacture of soap and candles.

Preparation.—(1.) By the action of superheated steam on fats:—

$$\underset{\text{Stearin}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\text{Water}}{3H_2O} = \underset{\text{Glycerin}}{C_3H_5(OH)_3} + \underset{\text{Stearic acid.}}{3C_{18}H_{36}O_2.}$$

Thus, glycerin may be prepared by merely distilling fat with superheated steam (see *Saponification by steam*), when decomposition occurs, the distillate, on standing, separating into two parts, the glycerine and the fatty acids, the fatty acids floating on the surface of the glycerin.

(2.) By the action of alkalies on fats (*saponification*). (*See* Soaps, Candles, etc.)

$$\underset{\text{Stearin}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\text{Sodic hydrate}}{3NaHO} = \underset{\text{Glycerin}}{C_3H_5(OH)_3} + \underset{\text{Sodic stearate.}}{3NaC_{18}H_{35}O_2.}$$

The glycerin solution, or "*spent lye*" as it is called (the stearate having been first rendered insoluble by the addition of sodic chloride), is drawn off, and distilled in a current of superheated steam. The water is removed from the distillate by evaporation.

Glycerin is formed in small quantity during the fermentation of sugar (p. 579).

(3.) Glycerin may be prepared synthetically, by digesting trichlorhydrine ($C_3H_5Cl_3$) (a compound formed by heating together propylene and iodine chlorides) with water in closed tubes at 338° F. (170° C.):—

$$\underset{\text{Trichlorhydrine}}{C_3H_5Cl_3} + \underset{\text{Water}}{3H_2O} = \underset{\text{Glycerin}}{C_3H_5(OH)_3} + \underset{\text{Hydrochloric acid.}}{3HCl.}$$

Properties.—(*a.*) *Physical.* A viscid liquid without color or smell. It has a sweet taste. Specific gravity 1·27. When pure and anhydrous, it crystallizes at a low temperature, the crystals melting at 60° F.

Action of heat.—At ordinary pressure, glycerin cannot be distilled without undergoing decomposition, when it changes to a dark color, and evolves (amongst other products) *acrolein* (C_3H_4O). When, however, it is distilled, either in vacuo at 410° F. (210° C.), or in an atmosphere of steam, it passes over undecomposed. It is soluble in water and in alcohol, but is insoluble in ether.

(*β.*) *Chemical.*—It has no reaction upon red or blue litmus, or other vegetable coloring matters. A solution of glycerin with yeast does not undergo vinous fermentation, but is gradually converted into propionic acid ($C_3H_8O_3 = C_3H_6O_2 + H_2O$). By the action of *dehydrating agents*, it forms *acrolein* ($C_3H_8O_3 = 2H_2O + C_3H_4O$). It combines with sulphuric acid to form *sulpho-glyceric acid* ($C_3H_8O_3,SO_3$), which acid forms soluble salts with lime and baryta. With a mixture of strong nitric and sulphuric acids it forms *nitroglycerin*, or *glonoin* (*Nobel's blasting oil*), ($C_3H_5(OH)_3 + 3HNO_3 = 3H_2O + C_3H_5(NO_2)_3O_3$, an oily and highly explosive liquid (*Specific gravity* 1·6). The monhydric *organic acids*, such as glacial acetic acid, when heated with it in closed tubes, form glycerides or *glyceric ethers*, as mon-, di-, or tri-acetin, as, *e.g.*, *monacetin*, $C_3H_5(OH)_2(C_2H_3O_2)$; in other words, compound ethers are formed where one, two, or three hydrogen atoms of the glycerin are replaced by an equivalent quantity of an acid radical. *Hydrochloric and hydrobromic acids* or the *compounds of phosphorus with chlorine or bromine*, form substitution compounds with glycerine, called mono-, di-, or tri-chlorhydrins or bromhydrins, where the group OH is replaced by chlorine or bromine; as *e.g.*, *Monochlorhydrine*, $C_3H_5Cl(OH)_2$, etc.

[Monochlorhydrine by the action of nascent hydrogen forms propylic glycol, $C_3H_6(OH)_2$.]

Hydriodic acid, when heated with glycerine to 100° C., produces an ether, which may be regarded as a double glycerin molecule, where four equivalents of (HO) are replaced by O_2, and a fifth by iodine ($C_6H_{10}O_2(HO)I$), but when heated to a higher temperature isopropylic iodide and allylic iodide are formed. Phosphorus iodide forms with glycerin, isopropylic iodide (C_3H_7I) and allylic iodide (C_3H_5I). By slow *oxidation* with nitric acid, glycerin forms *glyceric acid* ($C_3H_8O_3 + O_2 = C_3H_6O_4 + H_2O$), and by further action *oxalic acid* ($C_2H_2O_4$), which containing as it does fewer carbon atoms than glyceric acid, must be regarded as the result of its decomposition.

Pyrogallic Series.

SERIES II.—*Formula* $C_nH_{2n-9}(OH)_3$.

These alcohols, like the phenyls and orcins, are direct derivatives of benzene.

This series includes :—

	Formulæ.	Melting Point.	
		° F.	° C.
Pyrogallol	$C_6H_3(OH)_3$	239	115
Phloroglucin (*phloroglucol*)	$C_6H_3(OH)_3$	248	120

Pyrogallol ($C_6H_3(OH)_3$) (*Pyrogallic acid*). Melts at 239° F. (115° C.). Boils at 410° F. (210° C.).

Preparation.—(1.) By the action of heat on gallic acid :—

$$C_6H_2(OH)_3CO_2H = C_6H_3(OH)_3 + CO_2.$$

Gallic acid = Pyrogallic acid + Carbonic anhydride.

(2.) It may be collected as a crystalline sublimate on a paper covering when a dried watery extract of gall nuts is heated in a porcelain crucible.

Properties.—A crystalline body, soluble in water, alcohol, and in ether. It does not neutralize alkalies, nor does it form true salts. It melts at 239° F. (115° C.), boils at 410° F. (210° C.), and decomposes at 482° F. (240° C.), leaving a residue of metagallic acid ($C_6H_4O_2$). When dissolved in a strong potassic hydrate solution, it rapidly absorbs free oxygen (*see* page 121). With *pure* ferrous salts it forms a fine blue color, and with ferric salts a red color. Its use in photography as a "developer" depends on the property possessed by it of reducing gold, silver, and mercury from their salts. Distilled at a red heat over zinc dust, it yields benzene.

E.—HEXHYDRIC ALCOHOLS.

Formula $C_nH_{2n-4}(OH)_6$ Series.

This includes the three natural sugars: mannite, $C_6H_8(OH)_6$; dulcite, $C_6H_8(OH)_6$; and sorbite, $C_6H_8(OH)_6$.

Mannite (*Mannitol*), $C_6H_8(OH)_6$. *Natural History.*—Found in manna (the sap derived from different species of ash; *Fraxinus ornus*), and in other plants, such as seaweed, mushrooms, etc.

Preparation.—(1.) By the action of boiling alcohol on manna.

(2.) By the action of nascent hydrogen (sodium amalgam) on an aqueous solution of glucose ($C_6H_{12}O_6 + H_2 = C_6H_8(OH)_6$).

Properties.—Mannite crystallises in four-sided crystals, which are sweet to the taste, soluble in water and in alcohol, and insoluble in ether.

It does not ferment, thus differing from cane-sugar. It possesses no action on polarised light, nor does it reduce an alkaline solution of cupric hydrate on boiling, thus differing from grape-sugar.

Its relationship to the alcohols, and its hexatomic character, is marked as follows:—(1.) By the action upon it of nitric acid and of stearic acid [$C_{18}H_{35}O(OH)$] it forms *hexanitrate* and *hexastearate of mannite* respectively, six hydrogen atoms in these compounds being replaced in the former case by six of the group (NO_2), and in the latter by six of the radical of stearic acid ($C_{18}H_{35}O$).

$C_6H_8(OH)_6$;	$C_6H_8(ONO_2)_6$;	$C_6H_8(C_{18}H_{35}O_2)_6$.
Mannite;	Mannite hexanitrate;	Mannite hexastearate.

(2.) With *hydriodic acid*, mannite forms *iodohexane* ($C_6H_{13}I$), from which, by the action of argentic oxide and water, normal secondary hexylic alcohol may be obtained.

(3.) *By oxidation* (as by the action of platinum black) it yields *mannitic acid*, $C_6H_{12}O_7$, and *mannitose* ($C_6H_{12}O_6$) and (by the action of dilute nitric acid) *saccharic acid*, $C_6H_{10}O_8$, and ultimately oxalic acid.

Dulcite ($C_6H_8(OH)_6$) (*Dulcin; Dulcose; Melampyrite*) closely resembles its isomer mannite. It is obtained *naturally* from the expressed juice of the *melampyrum nemorosum;* and is prepared *artificially* by the action of nascent hydrogen on inverted milk-sugar.

By oxidation with nitric acid dulcite forms *mucic acid,* an isomer of saccharic acid.

Mercaptans or Thio-Alcohols.

The relationship subsisting between *potassic hydrate* (KHO) and *potassic sulphydrate* (KHS), has its counterpart in the relationship between an alcohol, as *ethylic alcohol* ($C_2H_5(OH)$), and a mercaptan or thio-alcohol, as *ethylic sulphydrate* ($C_2H_5(SH)$). The name *mercaptan* was originally applied solely to ethylic sulphydrate, which was the first discovered of these compounds, but it is now applied to the whole class of like bodies.

Preparation.—(1.) From *the corresponding alcohols;* By distillation with phosphorus pentasulphide :—

$5[C_2H_5(OH)]$	+	P_2S_5	=	$5[C_2H_5(SH)]$	+	P_2O_5.
Ethylic alcohol	+	Phosphorus pentasulphide	=	Ethylic sulphydrate	+	Phosphoric anhydride.

(2.) From *certain hydrocarbons.* By the action of potassic sulphydrate on their haloid derivatives. Thus :—

CH_3Cl	+	KHS	=	$CH_3(HS)$	+	KCl.
Methylic chloride	+	Potassic sulphydrate	=	Methylic sulphydrate	+	Potassic chloride.

The mercaptans are mostly offensive-smelling liquids, but some are solid. By the action upon their alcoholic solutions of certain *metals* (as K and Na), or of certain *metallic oxides* (as HgO) or of certain *salts* (as $HgCl_2$), the mercaptans form stable crystalline metallic derivatives, as *e.g.*, *potassic mercaptide* ($C_2H_5(KS)$, *mercuric mercaptide* ($(C_2H_5)_2(Hg''S_2)$), etc. *By oxidation with nitric acid,* the mercaptans form sulphonic acids.

SUPPLEMENTARY CHAPTER TO THE ALCOHOLS.

CARBO-HYDRATES.

The sugars, gums, starches, etc., are called carbo-hydrates, inasmuch as they contain hydrogen and oxygen in the proportions to form water combined with carbon. They may be arranged as follows:—Those that rotate the plane of polarisation to the right are marked +, and those that rotate it to the left —.

Group I.—Sucroses: *Composition* $C_{12}H_{22}O_{11}$.

1. Cane or sparkling sugar (sucrose or saccharose) +.
2. Milk sugar (lactose) +.
3. Melitose +. 4. Melizitose +. 5. Trehalose (or mycose) —. 6. Maltose +.

Group II.—Glucoses: *Composition* $C_6H_{12}O_6$.

1. Grape sugar (dextrose) +.
2. Fruit or mucoid sugar (lævulose) —.
3. Galactose +.
4. Sorbite +. 5. Eucalyn +. 6. Inosite 0.

Group III.—Amyloses: *Composition* $(C_6H_{10}O_5)_n$.

1. Starch +.
2. Dextrin +.
3. Glycogen +.
4. Mulin —.
5. Gums.
6. Cellulin.

GROUP I.—THE SUCROSES.

Formula $C_{12}H_{22}O_{11}$.

(1.) Cane or Sparkling Sugar ($C_{12}H_{22}O_{11}$).—*Sucrose.*

Natural History.—Found only in the vegetable kingdom, as *e.g.*, in the *sugar-cane* (saccharum officinarum), to the extent of 20 per cent.; the *Asiatic sugar-cane* (sorghum saccharatum), 9·5 per cent.; the *maple* (acer saccharinum), 5 per cent.; the *white beet*, 7 to 11 per cent.; the *date palm* (saguerus saccharifer); and *maize* (7·5 per cent.).

Probably sucrose is present in all plants just before flowering, at which time the soluble nutriment of the plant is most abundant.

Preparation.—(1.) The juice is first expressed from the plant. This is effected by *rollers* in the case of the sugar-cane, by *cutting* in the case of beet, by *tapping* in the case of the maple, etc.

(2.) The free acid of the juice is as soon as possible after extraction neutralized with lime, and heated to 140° F. (60° C.). A coagulum separates, containing albumen, earthy phosphates, etc. There must be *no delay* in this part of the process, otherwise the albumen present in the juice would set up fermentation, and cause a loss of sugar. The free acid *must be neutralized* with lime before boiling, otherwise it would, on boiling, convert a portion of cane into grape sugar, and loss be occasioned.

(3.) The clear liquor is now evaporated in open pans. (No doubt the large quantity of molasses formed is greatly due to this part of the operation.)

(4.) It is then crystallized in open wooden troughs, and at the same time briskly stirred, to prevent the formation of large crystals. The solid sugar formed is separated from the uncrystallizable syrup in casks with perforated bottoms. The former, dried in the sun, constitutes *raw* or *Muscovado sugar* (foots), and the latter *molasses.*

Sugar Refining.

(1.) The raw sugar is dissolved in water, and the solution in which a little lime, some ground bone-black (4 to 100 of sugar), and albumen, such as the serum of bullock's blood has been mixed, is then boiled by steam (blow up). The albumen, as it coagulates, rises to the surface, and carries with it the impurities suspended in the juice. The bone-black is added to assist in decolorising the solution.

(2.) The clear liquor is further decolorized by filtration through animal charcoal.

(3.) The colorless filtrate is now evaporated "in vacuo." By this means, the boiling point of the syrup is reduced from 230° F. (110° C.) to 150° F. (65·5° C.), that is, below the temperature at which heat injuriously affects sugar. The evaporation is continued until the syrup is sufficiently concentrated to "draw out."

(4.) The syrup is then run into coolers, and well stirred. So soon as crystallization commences, it is poured into moulds. After the sugar has set, the treacle is drained off, the sugar washed with a little clean syrup in order to remove adhering coloring matters, and the solid mass dried and polished in a lathe. This constitutes "loaf sugar."

It may be roughly stated that the raw sugar obtained is one-tenth the weight of the original juice, that is, about one-half the quantity of sugar the juice is known to contain. The raw sugar yields about 60 per cent. of pure cane sugar, the remainder consisting of water, uncrystallizable sugar, coloring matters, etc.

Properties.—(*a.*) *Physical.* Sugar is a colorless and sweet body, crystallizing in oblique rhombs; Sp. gr. 1·6. It rotates a ray of light to the right (73° 8′).

Action of heat.—(*a.*) *On dry sugar.*—Sugar melts at 365° F. (185° C.), changing *without loss of weight* into a mixture of dextro-glucose and lævulose ($C_{12}H_{22}O_{11}=C_6H_{12}O_6+C_6H_{10}O_5$). The action of this mixture on a ray of polarized light is directly opposite to that of cane sugar. Hence it is called *inverted sugar* (fruit sugar), the specific rotatory power of the lævulose being greater than the specific rotatory power of the dextro-glucose.

At from 365° to 400° F. (185° to 204·5° C.) the sugar gives off water and becomes discolored, forming "*toffy.*"

At from 400° to 420° F. (204·5° to 215·5° C.) it gives off more water, blackens, and leaves a brown residue called "*caramel*" ($C_{12}H_{18}O_9$).

Above this temperature it evolves inflammable and other gases (CO; CH_4; CO_2; etc.), a liquid distillate consisting of acetic acid, acetone, aldehyde, and a brown oil containing furfurol and assamar coming over. Charcoal only remains in the retort after the operation.

(*β.*) *On a solution of sugar and water.*—By boiling a solution of cane sugar, it becomes inverted sugar ($C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$). This change is assisted by the presence of certain salts and of dilute sulphuric or other mineral or organic acid. By prolonged boiling with dilute acids, brown products, such as *ulmin*, are formed.

Heated to 365° F. (185° C.) with a very little water, sugar becomes vitreous, and solidifies to an amorphous mass, called "*barley sugar*," an admixture of amorphous and crystallizable sugar. The amorphous sugar contained in barley sugar gradually becomes crystalline and opaque by keeping.

Solubility.—Sugar is soluble in cold water (1 in 2 aq. by weight), its solubility in boiling water being almost unlimited. It is almost insoluble in alcohol or in ether. Boiling absolute alcohol dissolves $\frac{1}{80}$th part of its weight, but gives it up again on cooling.

Action of acids.—Strong mineral acids rapidly decompose it. With *sulphuric acid* the sugar is completely decomposed, carbon being separated and SO_2 evolved. This reaction is peculiar to *cane* sugar. With *nitric acid*, oxalic and saccharic acids are formed. With *hydrochloric acid*, ulmin and ulmic acids are formed. With *nitro-sulphuric acid*, an amorphous, explosive, nitro-compound (*nitro-sucrose*) is formed ($C_{12}H_{18}(NO_2)_4O_{11}$). The action of weak mineral or vegetable acids is to convert sucrose, which is non-fermentable, into dextrose and lævulose, both of which sugars may be fermented.

Action of alkalies.—Concentrated solutions of the alkalies form with cane sugar bodies called *sucrates.* Dilute solutions act feebly and slowly, forming *ulmic acid.* Triturated with the dried caustic alkalies, sucrose does not turn brown, thereby distinguishing it from grape sugar.

Action of oxidizing bodies.—By oxidation with sulphuric acid and manganic peroxide, sugar yields *formic acid*, but when acted on with dilute nitric acid it yields saccharic and oxalic acids. Sucrose burns vividly when its mixture with potassic chlorate is touched with a drop of sulphuric acid. It fires when triturated with plumbic peroxide. It reduces silver and mercury salts by heat. Pure cupric hydrate is very slowly reduced by it even when the solution is boiling, but in the presence of an alkali a blue solution is formed, which, slowly and imperfectly, precipitates cuprous oxide on boiling.

A solution of sugar dissolves lead oxide. Lead also combines with sugar to form two crystalline *lead saccharates*, *viz.* $C_{12}H_{18}Pb_2O_{11}$ and $C_{12}H_{16}Pb_3O_{11}$.

Cane sugar does not ferment directly, but it does indirectly by conversion into dextrose and lævulose.

(2.) **Milk Sugar** (*Lactin* or *Lactose*) $C_{12}H_{22}O_{11}$.

Natural History.—Found only in animals (milk of mammalia).

Preparation.—From the *whey* of milk by evaporation and crystallization.

Properties.—(α.) *Physical.* A hard gritty substance, crystallizing in square prisms. It is not very sweet. It has a specific gravity of 1·5, and rotates a ray of light + 59° 3′.

Solubility.—Soluble in water (1 in 6 at 60° F.; 1 in 2·5 at 212° F.). It is insoluble both in alcohol and ether.

Action of heat.—At 284° F. (140° C.) two molecules of lactose lose one molecule of water. At 400° F. (204·5° C.) lactose fuses and loses more water. In other respects the action of heat upon it, corresponds to that on cane sugar.

(β.) *Chemical.* Milk sugar is decomposed by strong acids. Nitric acid, by oxidation, converts it into mucic, saccharic, tartaric and oxalic acids. Boiled with dilute acids, it is changed into a fermentable sugar called *galactose* ($C_6H_{12}O_6$), a body which, with nitric acid, forms mucic acid, and rotates a ray of light + 83° 3′. Lactose does not itself undergo vinous fermentation, but under the action of yeast rapidly changes to a fermentable sugar (galactose). Under the action of chalk and cheese lactose forms lactic acid, a certain quantity of alcohol being formed simultaneously. Boiled with an alkaline solution of cupric hydrate, it precipitates seven-tenths as much cuprous oxide as dextrose.

(3.) **Melitose** ($C_{12}H_{22}O_{11}$).—This is obtained from various species of eucalyptus. The crystals have a slightly saccharine taste. It is soluble in water (1 in 9 at 60° F.; 1 in 3 at 212° F.), and in boiling alcohol. It is dextro-rotatory 102°.

By the action upon melitose either of dilute sulphuric acid and heat, or of yeast, it forms two kinds of sugar—a fermentable sugar, *glucose*, and an unfermentable sugar, *eucalyn*. Nitric acid oxidizes it to mucic and oxalic acids. It does not reduce an alkaline copper solution.

(4.) **Melizitose** ($C_{12}H_{22}O_{11}$) is obtained from the larch. It is dextro-rotatory 94° 1′. With nitric acid, it forms oxalic acid. On boiling with dilute sulphuric acid it yields glucose. It ferments with difficulty.

(5.) **Trehalose** ($C_{12}H_{22}O_{11}$) is obtained from the trehala manna of Syria. It is dextro-rotatory 200°. It forms a detonating compound with strong nitric acid; with dilute nitric acid it forms oxalic acid. It ferments very imperfectly, and does not precipitate cuprous oxide from alkaline copper solutions.

(6.) **Mycose** ($C_{12}H_{22}O_{11}$) is obtained from ergot, mushrooms, etc. It is dextro-rotatory 173°. It ferments slowly.

GROUP II.—THE GLUCOSES.

Formula $C_6H_{12}O_6$.

(1.) **Grape Sugar** (*Glucose; Dextrose; Dextro-Glucose; Granular Sugar*) ($C_6H_{12}O_6$).

History.—Glucose occurs both in the vegetable and animal kingdoms. (*a.*) In the *vegetable* kingdom it is found in fossil ferns and in vegetable mould; in sweet fruits and in honey; in chestnuts; in growing potatoes and in malt. In ripe fruits and in honey, it usually occurs along with lævulose and cane sugar.

(β.) In the *animal* kingdom it is found in the urine, in minute quantity in health, but often in enormous quantity in diabetes. It also occurs in the liver and in the stomach during digestion.

Preparation.—(1.) From *fruits*, etc., by precipitating its solution in water with spirit. From *honey*, by washing with dilute alcohol, which dissolves the lævulose but leaves the glucose.

(2.) By the action of diastase (malt) on starch, or by merely boiling the starch in dilute sulphuric acid. The acid is to be neutralized with chalk, and the clear solution evaporated to a syrup and crystallized—

$$\underset{\text{Starch}}{C_6H_{10}O_5} + \underset{\text{Water}}{H_2O} = \underset{\text{Glucose.}}{C_6H_{12}O_6.}$$

Glucose is also formed by the action of dilute acids on cellulin.

(3.) By the action of dilute acids on the glucosides, such as æsculin, amygdalin, chitin, glycyrrhizin, salicin, etc.

Properties.—A granular non-sparkling body, forming nodular masses of minute acicular radiating crystals ($C_6H_{12}O_6,H_2O$). Its sweetening power is about one-half that of cane sugar. Specific gravity, 1·4. It is dextro-rotatory 54°.

Action of heat.—It suffers no decomposition up to 266° F. (130° C.). At 338° F. (170° C.) water is evolved, and *glucosan* ($C_6H_{10}O_5$) formed. By the further action of heat, it forms caramel.

It is soluble in water in all proportions. It is not soluble in spirit.

Action of acids.—Strong sulphuric acid converts grape sugar into sulpho-saccharic acid. (This acid forms a soluble baric salt.) *Nitric acid* oxidizes it to saccharic or oxalic acid. *Hydrochloric acid* decomposes it. Heated with *organic acids*, it forms conjugate acid compounds, such as tri-aceto-dextrose, $C_6H_9O_3(C_2H_3O_2)_3$. Boiled with *dilute sulphuric or hydrochloric acid*, it forms various brown compounds called ulmin, ulmic acid, etc.

Solutions of alkalies and alkaline earths decompose it even in the cold, but more rapidly when heated, forming a brown compound (Moor's Test). With yeast, it ferments rapidly and directly at a temperature of 77° F. (25° C.). It unites with certain salts (as NaCl) and metallic oxides (as CaO, BaO, etc.), forming with them unstable compounds such as $(C_6H_{12}O_6)_2NaCl.H_2O$ and $(C_6H_{12}O_6)_2(BaO)_3$, $2H_2O$, etc.

It is rapidly oxidized. Hence when boiled in alkaline solutions of silver and copper salts, it quickly reduces them, precipitating metallic silver or the red cuprous oxide. Five molecules of cuprous oxide are exactly reduced by one molecule of grape sugar.

(2.) **Lævulose** (*Lævo-glucose; Left-handed Glucose; Mucoid Sugar*) ($C_6H_{12}O_6$).

Natural History.—This sugar occurs, together with glucose, in honey, ripe fruits, etc.

Preparation.—(1.) By heating cane sugar with dilute acids, when a mixture of dextrose and lævulose (*i.e., inverted sugar*) is formed. On neutralizing with lime, calcium compounds of both glucose and lævulose result, the glucose compound being soluble in water, and the lævulose compound insoluble. The latter compound after separation is suspended in water, and decomposed by the action of carbonic anhydride or oxalic acid, whereby a pure lævulose is obtained.

(2.) By the action of dilute acids on inulin.

Properties.—A sweet syrup. It may be obtained as an amorphous solid, but with difficulty. It is more soluble than dextrose in water and in spirit. It rotates a ray of polarized light to the left. The rotation of glucose to the right is the same at all temperatures, but the extent of rotation to the left in the case of lævulose, varies with the temperature from 53 degrees at 194° F. (90° C.) to 106 degrees at 57·2° F. (14° C.).

Inasmuch as inverted sugar consists of *equal* parts of glucose (= + 56°) and lævulose (= — 106°), it follows that inverted sugar is lævo-rotatory (= — 50°). By heat lævulose forms a body isomeric with glucosan, called *lævulosan* ($C_6H_{10}O_5$). On oxidation lævulose yields saccharic acid. Its reaction with a ferment and with metallic salts are similar to those of glucose.

(3.) **Galactose** ($C_6H_{12}O_6$) is prepared by boiling milk sugar in dilute acids. It is dextro-rotatory 82° 3′. It ferments easily. It resembles glucose, except that, unlike it and all preceding sugars, it yields mucic acid on oxidation with nitric acid.

(4.) **Sorbite** ($C_6H_{12}O_6$) is prepared from the juice of the berries of the mountain ash. By oxidation with hot nitric acid, it forms oxalic acid. It does not yield alcohol by fermentation with yeast, but it yields lactic and butyric acids together with some alcohol by contact with cheese and chalk. It is dextro-rotatory 47°.

(5.) **Eucalyn** ($C_6H_{12}O_6$) is a sugar separated during the fermentation of eucalyptus sugar. It will not ferment, nor is it rendered fermentable by the action of dilute sulphuric acid. It is dextro-rotatory (+50°).

(6.) **Inosite** ($C_6H_{12}O_6$). The sugar of muscle. It is also found in kidney beans. Inosite is soluble in water, but insoluble in alcohol and ether. It does not undergo alcoholic fermentation, but forms lactic, butyric, and carbonic acids by the action upon it of chalk and cheese. It is without action on a polarized ray.

Glucosides.

There are various bodies found in plants, called *glucosides* (and which may be described as *compound ethers of glucose*); none of them have been prepared artificially. They yield on decomposition a sugar, together with other substances. The following are the most important of these bodies :—

(1.) **Amygdalin** ($C_{20}H_{27}NO_{11}+3H_2O$). *Source;* bitter almonds. Under the action of emulsion or synaptase forms glucose, bitter almond oil (*benzoic aldehyde*), and hydrocyanic acid. Thus :—

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} \;+\; \underset{\text{Water}}{2H_2O} \;=\; \underset{\substack{\text{Benzoic}\\\text{aldehyde}}}{C_7H_6O} \;+\; \underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{HCN} \;+\; \underset{\text{Glucose.}}{2C_6H_{12}O_6.}$$

(2.) **Æsculin** ($C_{21}H_{24}O_{13}$). *Source;* bark of horse-chestnut tree. Breaks up into dextrose ($C_6H_{12}O_6$), and æsculetin ($C_9H_6O_4$).

(3.) **Chittin** ($C_9H_{15}NO_6$). *Source;* wing-cases of insects.

(4.) **Glycyrrhizin** ($C_{24}H_{36}O_9$). *Source;* liquorice sugar.

(5.) **Indican** ($C_{26}H_{31}NO_{17}$). *Source;* wood. Yields dextrose and indigo blue (C_8H_5NO).

(6.) **Myronic Acid** ($C_{10}H_{19}NS_2O_{10}$). *Source;* black mustard. By the action of the myrosin (an albuminous ferment) present in the seed, the myronic acid (present as myronate of potassium), forms oil of mustard (*athylthiocyanate*), glucose, and sulphuric acid.

(7.) **Phlorizin** ($C_{21}H_{24}O_{10},2H_2O$). *Source;* root bark of apple and cherry-tree.

(8.) **Quercitrin** ($C_{33}H_{30}O_{17}$). *Source;* quercitron bark.

(9.) **Salicin** ($C_{13}H_{18}O_7$). *Source;* bark of willow, poplar; also found in the castoreum, contained in a gland of the beaver. Forms, under the action of synaptase or emulsin, dextrose ($C_6H_{12}O_6$) and salicylic alcohol (*saligenin*) ($C_6H_4(HO)CH_2OH$). By distillation with sulphuric acid and potassic bichromate, forms *salicylol* ($C_7H_6O_2$), or the artificial oil of the meadow sweet (*Spiræa ulmaria*). With dilute nitric acid, it yields *helicin* ($C_{13}H_{16}O_7$).

(10.) **Populin** ($C_{20}H_{22}O_8$). *Source;* bark of aspen.

(11.) **Ruberythric Acid** ($C_{26}H_{28}O_{14}$). *Source;* madder root.

(12.) **Solanin** ($C_{43}H_{71}NO_{16}$). *Source;* woody nightshade.

(13.) **Arbutin** ($C_{12}H_{16}O_7$). *Source;* leaves of the bear-berry (*arbutus uva ursi*).

(14.) **Coniferin** ($C_{16}H_{22}O_8$). *Source;* juice of *coniferæ*.

(15.) **Convolvulin** ($C_{31}H_{50}O_{16}$). *Source;* jalap root.

(16.) **Tannin** ($C_{27}H_{22}O_{17}$). *Source;* gall nuts. [The tannins constitute a group of substances.]

GROUP III.—AMYLOSES.

Starches: Fecula-Amidine.

Natural History.—The starches are organized, non-crystalline bodies, found in cells situate in every part of the vegetable, except the tips of the buds and the extremities of the rootlets. Starch is also found in animals, especially in embryonic tissue, as well as in the brain, liver, spleen, and kidneys of adults.

Preparation.—The tissue is first broken up, and the starch removed by washing with cold water, in which it is insoluble.

Varieties.—We may recognise four varieties:—

(1.) *Common starch;* (2.) *Lichen starch;* (3.) *Inulin;* (4.) *Paramylon.*

(1.) **Common Starch** ($(C_6H_{10}O_5)_n$).

Preparation.—(*a.*) From *wheat*, which contains 60 per cent. It is extracted either (1) by fermenting the wheat flour for three or four weeks, during which time the gluten putrefies, thereby assisting the separation of the starch (old method); or (2), by simple washing.

(β.) From *rice* (83 per cent.), extracted by washing the powdered rice with a weak alkaline lye to dissolve the gluten (Jones patent).

(γ.) From *potatoes* (20 per cent.), extracted by rasping and washing.

(δ.) From *arrowroot*, Jatropha manihot, etc.

Properties.—A white pulverulent crepitating solid. The form and size of the starch corpuscles vary with its source. It is insoluble in cold water, in alcohol or in ether. Specific gravity, 1·5.

Action of heat. (*a.*) *On the dry starch.* A moderate heat merely dries the starch corpuscles. A temperature of 320° F. (160° C.) discolors the starch a little, and renders it soluble (dextrin). At higher temperatures the starch becomes of a buff colour, and evolves water, leaving dextrin. At a still higher temperature, it evolves more water, and leaves caramel. At a still higher temperature, the starch is decomposed, a carbonaceous residue being formed, and carbonic and acetic acids, together with certain empyreumatic oils, evolved.

(β.) *Heated with water* to 158° F. (70° C.) the starch corpuscles split, and form with the water a thick paste, called *starch paste.* Boiled for a long time, this solution becomes clear. On the addition of alcohol to the clear solution, it deposits a white precipitate of soluble starch.

Action of acids.—All acids decompose starch; (α.) Strong *sulphuric acid* dissolves it, forming a compound acid. With dilute sulphuric acid starch is changed into glucose; (β.) *Concentrated nitric acid* converts starch into *xyloidin*, which is precipitated on the addition of water ($C_{12}H_{19}(NO_2)O_{10}$) to the acid solution. A weaker acid converts it into oxalic acid. A very weak acid changes it to dextrin. (γ.) *Hydrochloric acid* changes starch into glucose. The action of oxalic and tartaric acids (but not of acetic acid) is similar to that of hydrochloric acid.

Action of alkalies.—A cold alkaline solution forms a paste with starch. Fused with starch, the alkalies form oxalates.

Action of haloids.—Neither chlorine nor bromine have much action on starch in the cold, but when starch is heated in chlorine it is decomposed. The action of iodine is to color the starch blue, the color being destroyed at a little below 212° F.(100° C.), reappearing (if the heat has not been too great) as the solution cools. Ferments, such as yeast and diastase (like dilute sulphuric acid), change it into dextrin and glucose.

(2.) **Lichen Starch** is found in most lichens, such as Iceland and Carrageen moss. When boiled with water it forms a jelly. It is converted by acids into glucose. Iodine turns it a greenish brown color. It does not ferment when mixed with yeast or diastase.

(3.) **Inulin Starch** is found in the roots of most of the Compositæ, such as the dahlia, chicory, elecampane, etc. It is an amorphous white substance, decomposed, like starch, by heat. It forms dextrin by long-continued boiling. By the action of dilute acids, it yields lævulose. Iodine has no action upon it.

(4.) **Paramylon** (*glycogen*, or *animal starch*), is found in certain of the lower animals, and also in certain viscera of the higher animals, especially in the placenta. Acids change it into glucose. Iodine has no action upon it.

Uses.—In the *vegetable*, starch acts as a store of nutriment. In the *animal*, it serves the purpose of a respiratory food. The essential condition for rendering starch useful either to the vegetable or to the animal, is its conversion into soluble dextrin and sugar.

Gums ($C_6H_{10}O_5$).

Gums are organic bodies occurring in the juices of plants. They are amorphous, tasteless, and inodorous bodies. They are distinguished from *sugars* (α) by not being susceptible of fermentation, and (β) by forming *mucic acid* when oxidized with nitric acid. From *resins* they may be distinguished (α) by their solubility or by their softening in water, and (β) by their insolubility in alcohol.

Varieties.—*Dextrin, arabin, cerasin, tragacanthin, bassorin, calendulin, saponin, pectin, carrageenin, cydonin.*

(1.) **Dextrin** ($C_6H_{10}O_5$). Dextrin occurs in all vegetable juices, and may be prepared artificially (constituting artificial or British gum), either—

(α.) By heating starch with or without water.

(β.) By heating starch with dilute sulphuric acid.

(γ.) By the action on starch either of diastase (such as is contained in an infusion of malt), or of a similar compound such as is present in the stomach during digestion.

The properties of dextrine vary somewhat with its source. It dissolves in water, forming a mucilage, from which solution it is precipitated by alcohol and by acetate of lead. Its action on a ray of polarized light is dextro-rotatory (138° 7′).

Iodine colors some specimens of dextrin brown, whilst on others it has no action. When boiled with dilute acids it forms dextrose. It does not ferment with yeast. Pure gum does not reduce an alkaline copper solution.

(2.) **Arabin** ($C_{12}H_{22}O_{11}$) is the principle of gum arabic, and constitutes the soluble portion of other gums. It is soluble in its own weight of water, the solution being unacted upon by iodine. The arabin may be precipitated from its aqueous solution by alcohol, by basic acetate of lead, and by potassic silicate.

Gum-arabic is probably a lime salt, as it yields, on incineration, 3 per cent. of ash, which is almost entirely lime. Gummic acid is said to be soluble in water, like gum, but not to be precipitated from its solution by alcohol, unless an acid or a salt be present. It is lævo-rotatory 36°. By a heat of 212° F. (100° C.) it forms metagummic acid which is insoluble in water.

(2.) **Cerasin** ($C_6H_{10}O_5$) is the insoluble part of cherry-tree, peach, and other similar gums. It is said to be a compound of lime and metagummic acid. It is changed into arabin by long continued boiling.

(4.) **Tragacanthin** is the soluble portion of gum tragacanth.

(5.) **Bassorin** is the insoluble portion of gum tragacanth, and forms the chief part of gum bassora. It is soluble both in cold and boiling water.

(6.) **Pectin.**—Unripe fleshy fruits contain an insoluble body called *pectose*, to which the hardness of unripe fruits is due. By the action of a ferment present in the fruit, this body forms in the ripe fruit a soluble substance called *pectin.* The peculiarity of pectin is the property it possesses of forming a jelly with acids or alkalies. It is soluble in water, insoluble in alcohol, and without action on a polarized ray.

The solution of *pectin* is neutral. It is precipitated by alcohol, but not by plumbic acetate. By boiling with water it forms *parapectin* which is precipitated by plumbic acetate. By boiling with dilute acid it forms *meta-pectin*, which is acid to litmus, and is precipitated by barium chloride. By the action of bases, all these varieties of pectin are changed into pectic acid.

We are unable to fix definite formulas for these bodies.

REACTIONS TO BE NOTED.

Alcohol (Ethylic alcohol, $C_2H_5(OH)$) :—

1. Absorbs moisture. Mixes with water, heat and contraction of volume occurring at the time of admixture.

2. Heated in a test tube, (*α*.) volatilizes without blackening. (*β*.) The vapor has a peculiar odor, and (*γ*.) burns with a blue, smokeless, non-luminous flame.

3. Heated with sulphuric acid, (*α*.) alcohol does not blacken ; (*β*.) evolves an ethereal odor. [Methylated spirit turns brown.]

4. Heated with potassic hydrate it gives no action.

5. Heated with a solution of iodine in potassium iodide, and a little potash solution, a yellow crystalline precipitate of iodoform is produced.

Glycerin, $C_3H_5(OH)_3$:—

1. Heated in a test-tube glycerin decomposes without blackening, emitting acrid fumes of acrolein.

2. Its behaviour when heated with sulphuric acid or with potassic hydrate is similar to the action of heat without these reagents.

3. It has no action on vegetable colors.

4. Nitro-sulphuric acid forms with it the substitution compound nitro-glycerin ($C_3H_5(NO_2)_3O_3$).

Sugars :—

	Sucrose.	Glucose.
1. Taste	Very sweet	Not very sweet.
2. Action on polarized ray..	Dextro-rotatory 73·8°	Dextro-rotatory 54°.
3. Heated in a test tube ..	Chars ; odor of caramel	Chars.
4. Heated with H_2SO_4 ..	Chars rapidly ; SO_2 evolved	Chars slowly ; forms sulpho-saccharic acid.
5. Heated with potassic hydrate	No change	Becomes dark brown.
6. Heated with potassic cupric tartrate	No red ppt. of Cu_2O	Red precipitate of Cu_2O.
7. Add to the solution two drops of cupric sulphate, and then KHO	Turns blue ; on heating little alteration occurs at first ; a slight red precipitate falls after a time, but the blue color of the solution remains.	Turns blue ; on heating an immediate yellow precipitate occurs, becoming dark red (Cu_2O), the solution rapidly losing its color.

Starch:—

(1.) Under the microscope, starch cells appear as rounded grains, which polarize light.

(2.) Insoluble in cold water. When boiled the cells burst, and the starch forms a paste, shreds of membrane being apparent in the solution.

(3.) It forms a blue compound with free iodine; this compound is, (α.) soluble in pure water, and (β.) insoluble in solutions containing free acid; (γ.) is destroyed by heat, *temporarily* if the heat be slight, but *permanently* if the heat be considerable (p. 109.)

(4.) It is soluble in strong nitric acid, forming xyloidin.

Gum:—

1. Softens in cold water.
2. Gives no reaction with tincture of iodine.
3. Basic acetate of lead gives a white precipitate.

CHAPTER XXIV.

THE ORGANIC ACIDS.

Relationship to other Bodies. MONOBASIC ACIDS: Acetic—Acrylic—Sorbic—Benzoic—Cinnamic—Naphtoic. DIBASIC ACIDS: Succinic—Fumaric—Phthalic. TRIBASIC ACIDS: Tricarballylic—Mesitic. Reactions of the Acids.

SUPPLEMENTARY CHAPTER.—Fats and Oils—Soaps—Candles—The Tannins—Ink—Tanning.

ORGANIC ACIDS.

AN organic acid may be regarded as an alcohol derivative. It is a compound of a semi-molecule of hydroxyl (OH) with an oxygenated radical.

(1.) *An alcohol* is derived from a hydrocarbon by the substitution of one or more equivalents of the group (OH), for one or more equivalents of H. Thus—

C_2H_6 = *Ethane* and forms $C_2H_5(OH)$ *Ethylic alcohol.*
C_3H_8 = *Propane* „ „ $C_3H_7(OH)$ *Propylic alcohol.*

Upon the *number* of equivalents of (OH) substituted for hydrogen atoms depends the *atomicity* of the alcohol, by which we mean the number of ethers that an alcohol can form by the substitution of a monatomic alcohol radical for the hydrogen of the group (OH). Thus—

Monatomic alcohol	Diatomic alcohol	Triatomic alcohol.
$C_3H_7(OH)$	$C_3H_6(OH)_2$	$C_3H_5(OH)_3$.
Propyl alcohol;	*Propene alcohol;*	*Propenyl alcohol.*

(2.) *An organic acid* is derived from an alcohol by the equivalent substitution of O'' for H_2, or of O_2 for H_4, etc. Thus—

$C_2H_5(OH)$ *Ethylic alcohol* forms $C_2H_3O(OH)$ *Acetic acid;*
$C_3H_7(OH)$ *Propylic alcohol* „ $C_3H_5O(OH)$ *Propylic acid.*

(3.) An alcohol may yield more than one acid. The number of acids an alcohol is capable of forming may be determined by the number of times that the group (CH_2.OH) enters into the molecule of the alcohol. Thus—

Ethylic alcohol, $C_2H_5(OH)$, contains but *one* of the group CH_2OH ($+CH_3$). It therefore forms only *one* acid.

Ethene alcohol $C_2H_4(OH)_2$, contains *two* of the group CH_2OH. It therefore forms *two* acids.

(4.) But inasmuch as the change of an alcohol into an acid consists in the substitution of O for H_2, or in other words in the conversion of the group CH_2OH of the alcohol, into COOH in the acid (which latter group is termed *carboxyl*), it follows that the number of equivalents of carboxyl in the acid, determines the basicity of the acid; in other words, that the number of groups of carboxyl in the acid, indicates the number of hydrogen atoms that may be replaced by metals to form salts. Thus—

(α.) $C_2H_4O_2$ is *acetic acid*. It contains only *one* of the group COOH; it therefore is a *monobasic* acid, *i.e.*, only one atom of its hydrogen can be replaced by a metal in the formation of salts.

(β.) $C_2H_2O_4$ is *oxalic acid*. It contains *two* of the group COOH. It is therefore *dibasic*, *i.e.*, the molecule may have two atoms of its hydrogen replaced in the formation of salts, either by two of a monad metal, or by one dyad metal.

(5.) It is evident, therefore, that the basicity of any acid corresponds with the basicity of the alcohol from which such acid was derived. Many of the acids known have been actually derived from alcohols, whilst many, as yet, have not been classified.

Constitution of the Acids.—Acids have been regarded as formed on the type of a molecule of water by the substitution of an acid or oxygenated radical for *one* of the hydrogens (if the radical be univalent) of the water molecule, just as alcohols are regarded as formed on the type of a molecule of water by the substitution of an alcohol or hydrocarbon radical for *one* of hydrogen. If the radicals be divalent, the acids and alcohols are then regarded as formed on the double water type, etc. Thus—

$$(\alpha.)\ \left.\begin{matrix}H\\H\end{matrix}\right\}O = \text{Water};\quad \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O = \begin{matrix}\text{Ethylic}\\\text{alcohol};\end{matrix}\quad \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O = \begin{matrix}\text{Acetic}\\\text{acid.}\end{matrix}$$

(*single mol.*).

$$(\beta.)\ \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2 = \text{Water};\ \left.\begin{matrix}(C_3H_6)''\\H_2\end{matrix}\right\}O_2 = \begin{matrix}\text{Propene}\\\text{glycol};\end{matrix}\quad \left.\begin{matrix}C_3H_4O)''\\H_2\end{matrix}\right\}O_2 = \begin{matrix}\text{Lactic}\\\text{acid.}\end{matrix}$$

(*double mol.*).

The acid radicals are denoted by names ending in *yl*, as *acetyl*, the radical of acetic acid, etc.

Acid Derivatives.

(1.) **Salts.**—Organic salts (as we have said) are of different basicities, according to the number of times that the group CO.OH occurs in the molecule. When the acid is acted upon by a metallic carbonate, hydrate or oxide, the H of this group (carboxyl) is exchanged for a metal to form a salt.

(α.) *Monobasic acids*, such as acetic acid, $CH_3CO(OH)$, forms (1) *normal salts*, as sodium acetate, $CH_3CO(ONa)$; (2) *acid salts*, formed by the combination of a normal salt with a molecule of the acid, as acid potassium acetate, $(C_2H_3O)_2(OK)(OH)$; and (3) *basic salts*, formed by the combination of a normal salt with one or more molecules of a metallic oxide or hydrate, as triplumbic acetate, $Pb''(C_2H_3O_2)_2,2PbO$, etc.

(β.) *Dibasic acids*, such as oxalic acid, $C_2O_2(OH)_2$, form (1) *normal salts*, as ammonic oxalate, $C_2O_2(ONH_4)_2$, where all the displaceable hydrogen is replaced by a metal; and (2) *acid salts*, as acid ammonic oxalate, $C_2O_2(OH)(ONH_4)$, where one-half of the displaceable hydrogen is replaced by a metal.

(2.) **Acid Anhydrides or Oxides.**—These are bodies formed by the substitution of the hydrogen of the carboxyl in the acid, by an acid radical. Thus, $CH_3CO(OH)$ being acetic acid,—

(α.) $[CH_3CO(CH_3CO)O]$ = acetic oxide or anhydride.

(β.) $[CH_3CO(C_7H_5O)O]$ = acetobenzoic oxide.

Thus the acid radical may be the same as that already present in the body, as in (α), or it may be different, as in (β). Various mixed anhydrides may in this way be formed.

Preparation.—(1.) By the action of the acid chlorides either on the acids or on their salts.

(2.) By the action of acid chlorides on metallic oxides.

Properties.—(1.) By the action of *water*, the anhydrides become acids; (2) with *phosphoric chloride* (PCl_5), they form acid chlorides; (3) by the action of *alcohols*, they form ethereal salts; (4) with *ammonia*, they form acid amides.

(3.) **Acid Peroxides.**—These bodies bear the same relationship to acid oxides, that PbO bears to PbO_2. Thus:—

$(CH_3CO)_2O$ = *acetic oxide;* $(CH_3CO)_2O_2$ = *acetic peroxide.*

Preparation.—By the action of a metallic peroxide (as BaO_2) on an acid anhydride or chloride.

Properties.—The acid peroxides are powerful oxidising agents.

(4.) **Compound Ethers.**—(*Ethereal salts.*) Bodies formed by the substitution of the replaceable hydrogen of an acid by an alcohol (hydrocarbon) radical. Thus:—

Acetic acid, $CH_3CO(OH)$, forms $CH_3CO(OC_2H_5)$, *ethylic acetate.*

A similar formation takes place in the case of the mineral acids. Thus:—

Sulphuric acid, H_2SO_4, forms $(C_2H_5)_2SO_4$, *ethylic sulphate.*

Further, as we have normal and acid metallic salts, so also we may have normal and acid ethereal salts.

Preparation.—(1.) By the action of alcohols, either on the acids, the acid chlorides, or the anhydrides.

(2. By the action of the acid ethereal salts of sulphuric acid on the alkaline salts of the acids.

Properties.—Stable bodies. When heated with water they form the acid and the alcohol from which they were derived.

(5.) **Acid Chlorides, Bromides and Iodides.** These are bodies formed by the substitution of the (OH) in the carboxyl group of the acid, by either chlorine, bromine, or iodine. Thus—

Acetic acid, $CH_3CO(OH)$, forms $CH_3CO(Cl)$, *acetyl chloride.*

Succinic acid, $C_2H_4C_2O_2(OH)_2$, forms $C_2H_4C_2O_2(Cl_2)$, *succinyl chloride.*

Preparation.—By the action of the haloid phosphorus compounds on the acids, or on their metallic salts.

Properties.—Decomposed by water into the organic and haloid acids. Thus :—

$$CH_3CO(Cl) + H_2O = CH_3CO(OH) + HCl.$$

Acetyl chloride + Water = Acetic acid + Hydrochloric acid.

(6.) **Acid Amides.**—Bodies formed by the substitution of the (OH) in the carboxyl group of the acid by amidogen (NH_2). The monobasic acids yield normal amides only, whilst the dibasic acids yield both normal and acid amides. Thus :—

Acetic acid, $CH_3CO(OH)$, forms $CH_3CO(NH_2)$, *Acetamide* (neutral).

Succinic acid, $C_2H_4C_2O_2(OH)_2$, forms $C_2H_4C_2O_2(NH_2)(OH)$, *Succinamide* (acid).

" " " $C_2H_4C_2O_2(NH_2)_2$, *Succinamide* (neutral).

Preparation.—(1.) By the action of heat on the ammonium salts of the acids, whereby water is abstracted. Thus :—

$$CH_3CO(ONH_4) = CH_3CO(NH_2) + H_2O.$$

Ammonic acetate = Acetamide + Water.

(2.) By the action of ammonia either (α) on the compound ethers or (β) on the acid chlorides.

$$(\alpha.)\quad CH_3CO(OC_2H_5) + NH_3 = C_8H_5(OH) + CH_3CO(NH_2).$$

Ethylic acetate + Ammonia = Ethylic alcohol + Acetamide.

$$(\beta.)\quad CH_3CO(Cl) + 2NH_3 = NH_4Cl + CH_3CO(NH_2).$$

Acetyl chloride + Ammonia = Ammonic chloride + Acetamide.

Properties.—When the acid amides are heated with water, the ammonium salts are re-formed. When distilled with phosphoric anhydride, they become "nitriles" or alcoholic cyanides. Thus :—

$$CH_3CO(NH_2) + P_2O_5 = CH_3CN(\text{or}(C_2H_3)'''N) + 2HPO_3.$$

Acetamide + Phosphoric anhydride = Methyl cyanide (or ethenyl nitrile) + Phosphoric acid.

(7.) **Haloid Salts of the Acids.** These are compounds formed from the metallic salts, by the substitution of the metal by *chlorine*, etc. Thus :—

Potassic acetate, $CH_3CO(OK)$, forms $CH_3CO(OCl)$, *chlorine acetate.*

Properties.—Very unstable bodies. Explode at low temperatures.

(8.) Substitution Derivatives.—By the direct action of the haloid elements on the acids, the substitution of one or more chlorine atoms for hydrogen may be effected. Thus :—

$CH_3CO(OH)$ = Acetic acid.

$CH_2ClCO(OH)$ Monochloracetic acid.	$CH_2BrCO(OH)$ Monobromacetic acid.
$CHCl_2CO(OH)$ Dichloracetic acid.	$CHBr_2CO(OH)$ Dibromacetic acid.
$CCl_3CO(OH)$ Trichloracetic acid.	

These substitution acids form salts, compound ethers, acid chlorides, etc., like the original acid.

The organic acids are divided into three great classes according to the number of carboxyl groups (CO.OH) which they contain, or in other words, according to their basicity :—

I. Monobasic acids; II. Dibasic acids; III. Tribasic acids.

These may be further subdivided as follows :—

(A.) Monobasic Acids.

	SERIES.	Hydrocarbon from which derived.	Formula of Acids.	Example.
I.	Acetic series .. (fatty acids)	C_nH_{2n+2}	$C_nH_{2n+1}(COOH)$	Acetic acid $CH_3(COOH)$
	(α.) Lactic series ..		$C_nH_{2n}(OH)(COOH)$	Lactic acid $C_2H_4(OH)(COOH)$
	(β.) Pyruvic series		$C_nH_{2n-1}O(COOH)$	Pyruvic acid $C_2H_3O(COOH)$
	(γ.) Glyoxylic series		$C_nH_{2n-1}(OH)_2(COOH)$	Glyceric acid $(CH_2(OH)CH(OH)(COOH)$
II.	Acrylic series ..	C_nH_{n2}	$C_nH_{2n-1}(COOH)$	Acrylic acid $C_2H_3(COOH)$
III.	Sorbic series ..	C_nH_{2n-2}	$C_nH_{2n-3}(COOH)$	Sorbic acid $C_5H_7(COOH)$
IV.	Benzoic series ..	C_nH_{2n-6}	$C_nH_{2n-7}(COOH)$	Benzoic acid $C_6H_5(COOH)$
	(α.) Oxybenzoic series		$C_nH_{2n-8}(OH)(COOH)$	Salicylic acid $C_6H_4(OH)(COOH)$
	(β.) Dioxybenzoic series		$C_nH_{2n-9}(OH)_2(COOH)$	Oxysalicylic acid $C_6H_3(OH)_2(COOH)$
V.	(γ.) Gallic series ..		$C_nH_{2n-10}(OH)_3(COOH)$	Gallic acid $C_6H_2(OH)_3(COOH)$
	Cinnamic series ..	C_2H_{2n-8}	$C_nH_{2n-9}(COOH)$	Cinnamic acid $C_8H_7(COOH)$
	(α.) $C_nH_{2n-11}CO(OH)$		$C_nH_{2n-11}(COOH)$	Phenyl propiolic acid $C_6H_5C_2(COOH)$
VI.	Naphtoic series ..	C_nH_{2n-12}	$C_nH_{2n-13}(COOH)$	Naphtoic acid $C_{10}H_7(COOH)$
	(α.) $C_nH_{n2-19}CO(OH)$		$C_nH_{2n-19}(COOH)$	Anthracene-carboxylic acid $C_{14}H$ (COOH)

(B.) Dibasic Acids.

	SERIES.	Hydrocarbon from which derived.	Formula of Acids.	Example.
I.	Succinic series ..	C_nH_{2n+2}	$C_nH_{2n}(COOH)_2$	Succinic acid $C_2H_4(COOH)_2$
	(α.) Malic series ..		$C_nH_{2n-1}(OH)(COOH)_2$	Malic acid $C_2H_3(OH)(COOH)$
	(β.) Tartaric series		$C_nH_{2n-2}(OH)_2(COOH)_2$	Tartaric acid $C_2H_2(OH)_2(COOH)$
II.	Fumaric series ..	C_nH_{2n}	$C_nH_{2n-2}(COOH)_2$	Fumaric acid $C_2H_2(COOH)_2$
III.	Phthalic series ..	C_nH_{2-6}	$C_nH_{2n-8}(COOH)_2$	Phthalic acid $C_6H_4(COOH)_2$

(C.) Tribasic Acids.

SERIES.	Hydrocarbon from which derived.	Formula of Acids.	Example.
icarballylic series	C_nH_{2n+2}	$C_nH_{2n-1}(COOH)_3$	Tricarballylic acid $C_3H_5(COOH)_3$
sitic series ..	C_nH_{2n-6}	$C_nH_{2n-9}(COOH)_3$	Mesitic acid $C_6H_3(COOH)_3$

A. MONOBASIC ACIDS.

Acetic Series.

SERIES I. *Formula* $(C_nH_{2n+1}.(COOH))$.

Of these we recognise three groups—

(*a.*) *Normal or primary acids* $\left\{\begin{array}{l} C(C_nH_{2n+1})H_2 ; \\ (COOH) \end{array}\right.$

lerivatives of primary alcohols (*see* page 658), *i.e.*, an alcohol where ne hydrogen atom of carbinol $CH_3(OH)$ has been replaced by a adical of the formula C_nH_{2n+1}.

(*β.*) *Secondary acids* $\left\{\begin{array}{l} C(C_nH_{2+1})_2H \\ (COOH) \end{array}\right. ;$

lerivatives of secondary alcohols, *i.e.*, an alcohol where two hydrogen toms of carbinol $CH_3(OH)$ have been replaced by two radicals of he formula C_nH_{2n+1}.

(*γ.*) *Tertiary acids* $\left\{\begin{array}{l} C(C_nH_{2n+1})_3 \\ (COOH) \end{array}\right. ;$

lerivatives of tertiary alcohols, *i.e.*, an alcohol where three hydrogen toms of carbinol $CH_3(OH)$ have been replaced by three radicals of he formula C_nH_{2n+1}. Thus—

From the *alcohols* we obtain the *acids* :—

Alcohols.	Acids.	Example.
(*a.*) $C(C_nH_{2n+1})H_2(OH)$ Primary alcohol.	$\left\{\begin{array}{l} C(C_nH_{2n+1}H_2 ; \\ COOH \end{array}\right.$ Primary acid.	$\left\{\begin{array}{l} C(CH_3)H_2 \\ COOH \end{array}\right.$ Propionic or methacetic acid.
(*β.*) $C(_nCH_{2n+1})_2H(OH)$ Secondary alcohol.	$\left\{\begin{array}{l} C(C_nH_{2n+1})_2H ; \\ COOH \end{array}\right.$ Secondary acid.	$\left\{\begin{array}{l} C(CH_3)_2H \\ COOH \end{array}\right.$ Isobutyric or dimethacetic acid.
(*γ.*) $C(C_nH_{2n+1})_3(OH)$ Tertiary alcohol.	$\left\{\begin{array}{l} C(C_nH_{2n+1})_3 ; \\ COOH \end{array}\right.$ Tertiary acid.	$\left\{\begin{array}{l} C(CH_3)_3 \\ COOH \end{array}\right.$ Trimethacetic acid.

(*a.*) *Normal acids of the acetic series* $\left\{\begin{matrix} C(C_nH_{2n+1})H_2 \\ (COOH) \end{matrix}\right.$

ACIDS.	Formulæ.	Fusing Pt.		Boiling Pt.		Sp. Gr.	Molecular Weight.	Remarks.
		° F.	° C	° F.	° C.	° C.		
Formic acid .. (Methylic acid)	$H(COOH)$*	33·8	1	212·0	100	1·23 at 16	30	See page 700.
Acetic acid . .. (Ethylic acid)	$CH_3(COOH)$†	62·6	17	242·6	117	1·002 at 20	60	See page 701.
Propionic acid .. (Propylic acid)	$C_2H_5(COOH)$			285·8	141	·996 at 19	74	See page 704.
Butyric acid .. (Tetrylic acid)	$C_3H_7(COOH)$	below —4	— 20	321·8	161	·981 at 0	88	See page 704.
Valeric acid .. (Pentylic acid)	$C_4H_9(COOH)$			347·0	175	·957 at 0	102	See page 704.
Caproic acid .. (Hexylic acid)	$C_5H_{11}(COOH)$	41·0	5·0	388·4	198	·943 at 0	116	See page 705.
Œnanthylic acid (Heptylic acid)	$C_6H_{13}(COOH)$			413·6	212	·934 at 0	130	See page 705.
Caprylic acid .. (Octylic acid)	$C_7H_{15}(COOH)$	57·2	14·0	456·8	236		144	Occurs as a glyceride i butter of cow's milk cocoa nut oil.
Polargonic acid . (Nonylic acid)	$C_8H_{17}(COOH)$	64·4	18	500·0	260	·9065 at 17	158	Occurs in the leaves geranium, and may b pared by the action of acid on an oil of rue.
Capric acid .. (Rutic acid)	$C_9H_{19}(COOH)$	86·0	30				172	Occurs as a glyceride i ter, and also in coco oil, and in fusel oil. be prepared by the tion of oleic acid.
Lauric acid ..	$C_{10}H_{21}(COOH)$	110·4	43·6				200	Occurs as a glyceride fats of the bay tree, rim beans, cocoa n spermaceti, etc.
Myristic acid ..	$C_{13}H_{27}(COOH)$	128·8	53·8				228	Occurs as a glyceride i meg butter, cocoa n spermaceti, and otaba
Palmitic acid ..	$C_{15}H_{31}(COOH)$	143·6	62·0				256	See page 705.
Margaric acid ..	$C_{16}H_{33}(COOH)$	140·0	60·0				258	See page 706.
Stearic acid ..	$C_{17}H_{35}(COOH)$	156·5	69·2			1·01 at 0	284	See page 706.
Arachidic acid ..	$C_{19}H_{39}(COOH)$	167·0	75·1				312	A white crystalline fa pared by the saponifi of the oil of the ear (arachis hypogæa).
Behenic acid ..	$C_{21}H_{43}(COOH)$	168·8	76·0				340	A white crystalline fa pared by the saponifi of oil of ben.
Hyænasic acid ..	$C_{24}H_{49}(COOH)$	170·6	77·0					
Cerotic acid ..	$C_{26}H_{53}(COOH)$	172·4	78·0				410	Prepared from cerin that portion of bee soluble in boiling al or from Chinese wax produced on certain t China by the punctu species of coccus.
Melissic acid ..	$C_{29}H_{59}(COOH)$	190·4	88·0				452	Prepared by heating alcohol with potass drate.

* The radical $C(C_nH_{2n+1})H_2$ in formic acid is replaced by H.

† The value of the $_n$ in the general formulæ for acetic acid = 0.

Natural History (*General*).—Many of these acids are met with in nature *in a free state, e.g.*, formic acid is found in ants and in nettles, valeric acid in valerian root, etc. Certain of them occur naturally as *ethereal salts*, such as, *e.g.*, cetylic palmitate in spermaceti, glyceric stearate in beef and mutton fat, glyceric palmitate in palm oil, etc. (Hence the reason these acids are called the fatty series of acids.)

Preparation (*General*) :—

(1.) From *the corresponding primary alcohols.* By simple oxidation; such as by exposure to air on platinum black, by heating with a solution of chromic acid, etc.,

$$CH_3.CH_2OH \quad + \quad O_2 \quad = \quad CH_3.COOH \quad + \quad H_2O.$$

Ethylic alcohol + Oxygen = Acetic acid + Water.

(2.) From *the corresponding aldehydes.* By oxidation :—

$$CH_3.COH \quad + \quad O \quad = \quad CH_3.COOH.$$

Acetic aldehyde + Oxygen = Acetic acid.

(3.) From *the cyanides of the hydrocarbons* C_nH_{2n+1}. By the action upon them either of acids or alkalies :—

(*a*.) $C_nH_{2n+1},CN + 2H_2O + HCl = C_nH_{2n+1},(COOH) + NH_4Cl.$

(*β*.) $C_nH_{2n+1},CN + H_2O + KHO = C_nH_{2n+1},(COOK) + NH_3.$

[The cyanides are formed by the action of potassic cyanide on a haloid derivative of a hydrocarbon, and in some cases by distilling potassic cyanide with the potassic salts of the sulphonic acids.]

(4.) By the action of carbonic anhydride on a compound of the alcohol radicals of the methyl series with potassium or sodium. Thus :—

$$CH_3Na \quad + \quad CO_2 \quad = \quad CH_3.CO(ONa).$$

Sodium methide + Carbonic anhydride = Sodium acetate.

(5.) By the action of water on the corresponding acid chlorides. Thus :—

$$C_2H_3OCl \quad + \quad H_2O \quad = \quad HCl \quad + \quad CH_3.COOH.$$

Acetyl chloride + Water = Hydrochloric acid + Acetic acid.

General Reactions of the Acids of the Acetic Series.

1. When these acids are submitted to electrolysis, the nascent oxygen evolved from the positive pole sets free the radical and resolves the carboxyl into water and carbonic anhydride $(2(CH_3.CO.OH) + O = (CH_3)_2 + 2CO_2 + H_2O)$.

2. When the ammonic salt of these acids is heated with phosphoric anhydride, the salt parts with its water, and forms a nitrile or cyanide of the alcohol radical next below it. Thus :—

$$CH_3.CO(ONH_4) \quad + \quad 2P_2O_5 \quad = \quad CH_3(CN)''' \quad + \quad 4HPO_3.$$

Ammonic acetate + Phosphoric anhydride = Methylic nitrile + Metaphosphoric acid.

3. By distilling the potassic salt of an acid of the acetic series with an equivalent quantity of potassic formate, the acid is converted into the aldehyde. Thus :—

$$CH_3CO(OK) \quad + \quad HCO(OK) \quad = \quad CH_3COH + \quad K_2CO_3$$

Potassic acetate + Potassic formate = Acetic aldehyde + Potassic carbonate.

When this aldehyde is treated with nascent hydrogen it is converted into a primary alcohol.

4. By the distillation of the dry baric or calcic salt of an acid, a ketone is formed. Thus :—

$$Ca(C_2H_3O_2)_2 = CO(CH_3)_2 + Ca''CO_3.$$

Calcic acetate = Acetone + Calcic carbonate.

When the ketone is treated with nascent hydrogen it is converted into a secondary alcohol.

5. By heating the acids and the alcohols together in sealed tubes, the compound ethers are formed (*see* page 694).

We now proceed to examine the acids in detail.

Formic Acid (HCOOH)=(CH_2O_2). *Molecular weight,* 46. *Specific gravity of liquid,* 1·23. *Fuses at* 33·8° F. (1°C.), *and boils at* 212° F. (100° C.).

Synonyms.—Methylic acid; Hydric formate.

Natural History.—It constitutes the active principle of the stinging matter of ants, nettles, etc.

Preparation.—(1.) By the oxidation of methylic alcohol :—

$$CH_3(OH) + O_2 = H(COOH) + H_2O.$$

Methylic alcohol + Oxygen = Formic acid + Water.

(2.) By the oxidation of numerous organic bodies, such as gum, sugar, starch, etc.

[Formic acid may be conveniently prepared by distilling cautiously and in a large retort a mixture of sugar (1 part), manganese dioxide (2 parts), water (6 parts), and sulphuric acid (3 parts). This distillate must be neutralized with carbonate of soda, the resulting crystalline sodium formate being decomposed with sulphuric acid. From this a solution of formic acid may be obtained by distillation. The anhydrous acid may be prepared by saturating the solution so prepared with lead oxide and decomposing the dried lead formate with dry sulphuretted hydrogen.]

(3.) By the action of heat on oxalic acid. (The acid should in the first place be mixed with sand or glycerine.)

$$C_2H_2O_4 = H(COOH) + CO_2$$

Oxalic acid = Formic acid + Carbonic anhydride.

(4.) By the action of water vapor and carbonic anhydride on potassium, the potassic salt of formic acid is produced.

$$K_2 + 2CO_2 + H_2O = HCO(KO) + KHCO_3.$$

Potassium + Carbonic anhydride + Water = Potassic formate + Hydric potassic carbonate.

(5.) When silent electrical discharges are passed through a mixture of hydrogen and carbonic anhydride, traces of formic acid are said to be produced. (Brodie.)

(6.) By the action of potassic hydrate (α) on *chloroform,* (β) on *carbonic oxide,* and (γ) on *hydrocyanic acid.*

(α.) $CHCl_3 + 4KHO = HCO(KO) + 3KCl + 2H_2O.$
Chloroform + Potassic hydrate = Potassic formate + Potassic chloride + Water.

(β.) $CO + KHO = HCO(OK).$
Carbonic oxide + Potassic hydrate = Potassic formate.

(γ.) $HCN + KHO + H_2O = HCO(OK) + NH_3.$
Hydrocyanic acid + Potassic hydrate + Water = Potassic formate + Ammonia.

Properties.—(α.) *Physical.* The anhydrous acid is a colorless, inflammable, corrosive liquid, burning with a blue flame. The vapor has a very penetrating odor. Sp. Gr. 1·23. When cooled to below 32° F. (0° C.) it forms brilliant tabular crystals. It boils at 212° F. (100° C.). It dissolves in water freely, the solution having a very acid reaction. It decomposes carbonates readily. By the action of alcohol it may be partially converted into ethyl formate.

(β.) *Chemical.* With *sulphuric acid,* formic acid breaks up into water and carbonic oxide ($CH_2O_2 = H_2O + CO$); with *strong bases* it forms oxalic acid, hydrogen being evolved ($2HCO(OH)) + BaO = C_2O_2(BaO_2) + H_2 + H_2O$). With *chlorine,* it forms hydrochloric acid and carbonic anhydride ($HCO(OH) + Cl_2 = 2HCl + CO_2$); with *water,* it forms a hydrate ($CH_2O_2 + H_2O$) which remains liquid at low temperatures.

Formic acid is a powerful reducing agent. Thus it converts mercuric chloride into mercurous chloride (calomel), and reduces metallic mercury when mixed with mercuric oxide, metallic silver from the nitrate, etc. ($HCO(OH) + HgO = CO_2 + Hg + H_2O$). This reducing action of formic acid on metallic salts, distinguishes it from all other acids (such as acetic acid) of this group. It is also a powerful antiseptic, preventing putrefaction.

It forms salts called formates, all of which are soluble, and may be expressed by the formulæ, $HCO_2.M'$; $(HCO_2)_2M''$; $(HCO_2)_3M'''$, etc.

Acetic Acid = ($C_2H_4O_2 = CH_3(COOH)$). *Molecular weight,* 60. *Specific gravity,* 1·063. *Fuses at* 62·6° F. (17° C.), *and boils at* 246·2° F. (119° C.).

Synonyms.—Ethylic acid; Hydric acetate; Spirits of vinegar.

Natural History.—It occurs in small quantities in animal fluids, and also in the juices of plants.

Preparation.—(1.) By the general processes already described (page 699).

(2.) It is also produced during the destructive distillation of wood (*see* page 597); and

(3.) During the (so-called) acetous fermentation.

[In Germany vinegar, which contains 5 to 15 per cent. of pure acetic acid, is prepared by mixing dilute alcohol with a little yeast and allowing the mixture to flow over wood shavings steeped in vinegar, the whole being exposed to a free current of air. Another method is by placing some vinegar in a large empty cask, to which free access of air is permitted at a temperature of 35° C. Wine is added at intervals so soon as the spontaneous acidification of the previous addition has been effected. English vinegar is made from a malt beer (without hops) by its passage through a vat filled with bundles of twigs, an arrangement being made for a free current of air through the vat. All these oxidation processes are assisted (to say the least) by the presence of the *Mycoderma aceti.* A little sulphuric acid is added to the finished article to prevent "*mothering.*"]

Glacial acetic acid ($C_2H_4O_2$) is prepared by distilling sodic acetate with concentrated sulphuric acid.

Properties.—Acetic acid is a colorless, pungent, corrosive liquid, solidifying to a white crystalline mass at 62·6° F. (17° C.) and boiling at 246·2 F. (119° C.). Sp. Gr. 1·063. The vapor is inflammable.

Its vapor density exhibits an anomalous behaviour. Thus, at a very high temperature, its vapor has a normal density of 30, or half its molecular weight (Mol. Wt. 60), whilst at a few degrees above its boiling point, the vapor has the abnormal density of 45. This is explained by supposing that at the lower temperature the vapor is not a true gas, but commences at this low temperature, so to speak, to behave as a liquid.

It mixes with alcohol, ether, and water, in all proportions. On the addition of water its specific gravity rises, until the proportions correspond to a hydrate of the formula $C_2H_4O_2,H_2O$. By adding more water the specific gravity sinks. The acid dissolves camphor, etc. When potassic acetate is distilled with arsenious oxide, it yields the fetid inflammable body called arsendimethyl or kakodyl ($As_2(CH_3)_4$).

Metallic Salts of Acetic Acid.

Of these the following are the most important :—

Names.	Formulæ.	Remarks.
Potassic acetate, normal ..	$KC_2H_3O_2$	A deliquescent salt, soluble in water and alcohol.
,, acid ..	$KC_2H_3O_2,C_2H_4O_2$	Decomposes at 392° F. (200° C.), giving off the glacial acid.
Sodic acetate	$NaC_2H_3O_2,3H_2O$	Melts at 550·4° F. (288° C.); decomposes at 599° F. (315° C.).
Ammonic acetate, neutral	$NH_4C_2H_3O_2$	*Spiritus Mindereri* is the aqueous solution of this salt.
,, acid ..	$NH_4C_2H_3O_2,C_2H_4O_2$	Prepared as a crystalline sublimate by heating a mixture of ammonium chloride and potassium acetate.

Names.	Formulæ.	Remarks.
lumbic acetate, normal.. (Sugar of lead)	$Pb''(C_2H_3O_2)_2 3H_2O$	Prepared by dissolving litharge in acetic acid.
,, basic	$2Pb''(C_2H_3O_2)_2.PbO$ $Pb''(C_2H_3O_2)_2 2PbO$	The solution constitutes goulard water.
ıpric acetate, normal ..	$Cu''(C_2H_3O_2)_2+aq$	
,, basic (verdigris)	$2Cu''(C_2H_3O_2)_2CuO,6H_2O$ $Cu''(C_2H_3O_2)_2,2CuO,3H_2O$	
lver acetate	$Ag(C_2H_3O_2)$	
luminic acetate, neutral	$(Al_2)^{vi}(C_2H_3O_2)_6$	Much used in calico printing, the acetic acid escaping at a moderate heat. Prepared by mixing solutions of lead acetate and alum.
,, basic..	$Al_2O_3,2C_4H_6O_3,4H_2O$	
errous acetate	$Fe''(C_2H_3O_2)_2$	
erric acetate	$(Fe_2)^{vi}(C_2H_3O_2)_6$	
nc acetate	$Zn''(C_2H_3O_2)_2 2H_2O$	

Further important derivatives of acetic acid are stated in the following table :—

Derivatives of Acetic Acid.

Names.	Formulæ.	Sp. Gr.	Boiling Pt.		Remarks.
			°F.	°C.	
lic acetate	$CH_3CO(OCH_3)$	0·9562	131·	55·5	Soluble in alcohol, water, and ether.
c acetate .. .. (Acetic ether).	$CH_3CO(OC_2H_5)$	0·890	170·	77·0	With ammonia it yields *acetamide*. Hydrogen is said to be evolved when ethylic acetate is heated with sodium.
c acetate	$CH_3CO(OC_5H_{11})$		300·2	149·0	Odor of Jargonelle pear.
c chloride .. .. etyl chloride).	CH_3COCl		131·0	55·0	A colorless liquid, decomposed by water. Prepared by the action of PCl_5 on glacial acetic acid.
anhydride ..	$\left.\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\right\}O$		280·4	138·0	A heavy oil; prepared by the action of acetyl chloride on potassic acetate
peroxide	$\left.\begin{matrix}CH_3COO\\CH_3COO\end{matrix}\right\}$				Prepared by the action of BaO_2 on acetic anhydride.
hloracetic acid..	$CH_2Cl.COOH$		366·8	186·0	Prepared by the action of chlorine on glacial acetic acid in sunlight. A solid body, melting at 147·2° F. (61° C.).
racetic acid ..	$CHCl_2COOH$	1·5216	221·0	105·0	Prepared by exposing monochloracetic acid to the action of dry chlorine. A liquid.
oracetic acid ..	$CCl_3.COOH$	1·617 of fused acid.	390·2	199·0	Prepared by exposing a little of the crystallized acid in a bottle of chlorine to sunlight for several hours. A solid body, melting at 114·8° F. (46° C.).
romacetic acid..	$CH_2BrCOOH$				These acids are prepared by heating bromine with glacial acetic acid in sealed tubes.
nacetic acid ..	$CHBr_2COOH$				
macetic acid ..	CBr_3COOH				
tic acid	$CH_3CO(SH)$		203·0	95·0	Prepared by distilling together acetic acid and P_2S_5. A colorless liquid.
tic acid	$CH_2ICO(OH)$				
uide	$CH_3CO(NH_2)$		429·8	221·0	A solid, melting at 172·4° F. (78° C.). Prepared by the distillation of ammonic acetate. It combines with acids, and yields metallic derivatives
acetic acid.. .. cocine, Glycocol).	$CH_2(NH_2)CO(OH)$				A solid, formed by the action of ammonia on bromacetic acid.
l glycocine.. .. (Sarcocine).	$C_3H_7NO_2$				Prepared either by digesting ethyl chloracetate with an excess of a concentrated solution of methylamine, or by boiling kreatine with baryta water.

Propionic Acid ($C_3H_6O_2=C_2H_5COOH$). *Molecular weight*, 74. *Boils at* 284° F. (14° C.).

Synonyms.—Methacetic acid; Propylic acid.

Preparation.—(1.) By the general methods already described (p. 699). [It is usually prepared by the action of acids or alkalies on ethylcyanide.]

(2.) By the action of hydriodic acid on lactic or glyceric acids ($C_3H_6O_3+2HI=C_3H_6O_2+H_2O+I_2$).

(3.) By the fermentation either of glycerine or of sugar with putrid cheese, in the presence of calcic carbonate.

Properties.—A colorless liquid, boiling at 284° F. (140° C.). It is soluble in water. It forms salts called propionates.

Butyric Acid ($C_4H_8O_2=C_3H_7(COOH)$). *Molecular weight*, 88. *Specific gravity of liquid*, 0·9886. *Fuses below* –4° F. (–20° C.). *Boils at* 321·8° F. (161° C.).

Synonyms.—Ethacetic acid; Diethacetic acid; Tetrylic acid.

Natural History.—It is found in butter, in tamarinds, in various animal secretions, in various kinds of decomposing animal and vegetable matters, etc.

Varieties.—The acid is known in two isomeric conditions; viz., as *normal butyric acid* ($CH_3.CH_2.CH_2.(COOH)$), and as *isobutyric aci* $CH(CH_3)_2(COOH)$. They are both colorless liquids, and, when heated yield acetic acid and carbonic anhydride.

Preparation of (*a*) *normal butyric acid.*—(1.) By the oxidation o normal butylic alcohol ($CH_2.CH_2.CH_3.CH_2.OH$).

(2.) By the fermentation of sugar with cheese and chalk, the latte being added to neutralize the acid as fast as it is formed.

Properties.—At 32° F. (0° C.) it has a Sp. Gr. of 0·981. It boils a 323·6° to 325·4° F. (162° to 163° C.).

Preparation of (*β*) *isobutyric acid.*—By the oxidation of isobutyli alcohol ($CH(CH_3)_2CH_2OH$).

Properties.—At 0° C. it has a Sp. Gr. of 0·959. It boils at 309·2° F (154° C.). It is more easily decomposed by heat and has a less dis agreeable odour than the normal acid.

Valeric Acid, $C_5H_{10}O_2=C_4H_9.(COOH)$. *Molecular Weight*, 10 *Sp. Gr. of liquid*, 0·937. *Boils at* 347° F. (175° C.).

Synonyms.—Valerianic acid; Pentylic acid.

Natural History.—It is found in valerian root, in the berries of th guelder rose, and in many other plants.

Varieties.—It exists in four isomeric states, *viz.*—

(*a.*) *Normal valeric* or *valerianic acid* (propylacetic acid)—

$$CH_3.CH_2.CH_2.CH_2.(COOH).$$

Preparation.—By the oxidation of normal amylic alcohol.

Properties.—An oily liquid, having an acid taste, burning with smoky flame, and boiling at 365° F. (185° C.). It has a speci gravity of 0·9577 at 32° F. (0° C.).

(β.) *Iso-valeric acid* (iso-propylacetic acid) $CH(CH_3)_2.CH_2.(COOH)$.

Preparation.—By the oxidation of iso-amylic alcohol.

Properties.—A liquid boiling at 347° F. (175° C.). It has a specific gravity at 0° C. of 0·9468.

(γ.) The third modification of this acid has not, as yet, been prepared. Its suggested formula is $CH(CH_3)(C_2H_5)CO.(OH)$ (methethacetic acid). Unlike the other acids, it rotates a ray of light to the right.

(δ.) *Tertiary valeric acid* (trimethacetic acid) $C(CH_3)_3(COOH)$.

Preparation.—From tertiary butylic alcohol.

Properties.—A white crystalline body, melting at 95° F. (35° C.), and boiling at 321·8° F. (161° C.).

Valeric acid forms metallic and ethereal salts, called valerates, and also substitution compounds, such as chlorovaleric acid ($C_5H_7Cl_3O_2$).

Caproic Acid, $C_6H_{12}O_2=C_5H_{11}.(COOH)$. *Molecular Weight,* 116. *Sp. Gr. at* 32° F. (0° C.) 0·943. *Solidifies at* 15·8° F. (–9° C.). *Boils at* 388·4° F. (198° C.).

Synonym.—Hexylic acid.

Natural History.—It occurs as a glyceride in the butter of cows' milk, and also in cocoa-nut oil.

Preparation.—(1.) By the action of alkalies on amyl cyanide ($C_5H_{11}.CN$).

(2.) By the oxidation of poppy oil, of casein, and of many fatty acids.

(3.) By the saponification of cocoa-nut oil, and distilling the soap formed with dilute sulphuric acid.

Properties.—A clear oil. It forms salts called *caproates.*

Leucine, or *Amido-caproic acid,* $C_6H_{13}NO_2$, or $C_6H_{11}(NH_2)O_2$, is formed by the decomposition of, or by the action of acids and alkalies on, various animal substances. It may be obtained by the action of ammonia on bromo-caproic acid. It consists of volatile crystalline scales, which melt at 212° F. (100° C.).

Œnanthylic Acid, $C_7H_{14}O_2$, or $C_6H_{13}(COOH)$. *Molecular weight,* 130. *Sp. Gr. at* 32° F. (0° C.) 0·934. *Boils at* 413·6° F. (212° C.).

Synonym.—Heptylic acid.

Preparation.—By the oxidation either of castor oil or of œnanthylic aldehyde ($C_7H_{14}O$), a body obtained from castor oil by dry distillation.

Palmitic Acid, $C_{16}H_{32}O_2$, or $C_{15}H_{31}(COOH)$. *Molecular weight,* 256.

Natural History.—It occurs in many, if not in most natural fats, as a glyceride, associated with stearin, as, *e.g.*, in palm oil, as glyceric palmitate ; in spermaceti, as cetyl palmitate ; in bees' wax, as myricyl palmitate (melissin), etc.

Preparation.—(1.) By saponifying palm oil, and decomposing the soap formed with sulphuric acid.

(2.) By melting oleic acid with potassic hydrate.

Properties.—A colorless, odorless, tasteless body, insoluble in water. It forms normal, and in some cases (as with K and Na) acid metallic salts ($M'C_{16}H_{31}O_2$, or $M''(C_{16}H_{31}O_2)_2$.) It also forms ethereal salts, such as glyceryl palmitates or palmatins.

Margaric Acid, $C_{17}H_{34}O_2$, or $C_{16}H_{33}(COOH)$. *Molecular weight*, 258.

History.—This name was originally applied to an acid, obtained by the saponification of natural fats. It is now proved, however, that what was originally called margaric acid, is a mixture of stearic with palmitic or other acids. The name margaric acid is applied, however, to an acid produced by the following reaction.

Preparation.—By the action of an alcoholic solution of potassic hydrate on cetyl cyanide, the resulting potassium salt being decomposed with dilute hydrochloric acid.

Stearic Acid, $C_{18}H_{36}O_2=C_{17}H_{35}(COOH)$. *Molecular weight*, 284.

Natural History.—A constituent of solid animal fats, such as suet. Always occurs in nature as a glyceride in conjunction with palmitic acid. It is also found in certain vegetable fats, such as the fat of cacao beans, the berries of the cocculus Indicus, etc.

Preparation.—The fat is first saponified with an alkali, and the compound so formed decomposed by heating with dilute sulphuric acid. The free acid is then dissolved in alcohol and crystallized. It may be separated from the palmitic acid accompanying it as an insoluble magnesic stearate.

Properties.—A white crystalline body, melting at 156·5° F. (69·2° C.). Distils unchanged. Forms ethereal salts, and also metallic salts called stearates, most of which are insoluble.

See SUPPLEMENTARY CHAPTER FOR FATS, OILS, etc.

Lactic Series.

SERIES I. (*a.*)—*Formula* $C_nH_{2n}(OH)COOH$.

The acids of this series are monobasic dihydric acids. They are derivatives of the acetic acid series, one hydrogen being replaced by one semi-molecule of hydroxyl. Thus—

$C_nH_{2n+1}COOH$ — $C_nH_{2n}(OH)COOH.$
Acid of acetic series — Acid of lactic series.

Varieties.—(Each variety includes both normal and iso-acids.)

1. *Primary acids* $\left\{\begin{array}{l} C(C_nH_{2n+1})H.OH \\ CO.OH \end{array}\right.$
2. *Secondary acids* . $\left\{\begin{array}{l} C(C_nH_{2n+1})_2.OH \\ CO.OH \end{array}\right.$
3. *Primary olefine acids* $C_nH_{2n}\left\{\begin{array}{l} CH_2OH \\ CO.OH \end{array}\right.$

4. *Secondary olefine acids* $C_nH_{2n}\left\{\begin{matrix}C(C_nH_{2n+1})H.OH\\ CO.OH\end{matrix}\right.$

5. *Tertiary olefine acids* $C_nH_{2n}\left\{\begin{matrix}C(C_nH_{2n+1})_2OH\\ CO.OH\end{matrix}\right.$

The following acids belong to the lactic series :—

Name.	Formulæ.	Molecular Wt.
Carbonic acid	$CO(OH)_2$	62
Glycollic acid	$(CH_2OH)(COOH) = C_2H_4O_3$	76
Lactic acid	$C_2H_4(OH)(COOH) = C_3H_6O_3$	90
Oxybutyric acid (Butylactic acid) ..	$C_3H_6(OH)(COOH) = C_4H_8O_3$	114
Oxyvaleric acid (Valero-lactic acid) ..	$C_4H_8(OH)(COOH) = C_5H_{10}O_3$	128
Oxy-caproic acid (leucic acid)	$C_5H_{10}(OH)(COOH) = C_6H_{12}O_3$	132
Amylhydro-oxalic acid	$C_6H_{12}(OH)(COOH) = C_7H_{14}O_3$	146
Diamyloxalic acid	$C_{11}H_{22}(OH)(COOH) = C_{12}H_{24}O_3$	216

General Preparation of the Normal Acids of the Lactic Series.

(1.) *From the glycols* (*i.e.*, a dihydric alcohol, such as $C_2H_4(HO)_2$ (glycol)). By oxidation with nitric acid, platinum black, etc.

$$\underset{\text{Glycol}}{CH_2(OH).(CH_2OH)} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Glycollic acid}}{CH_2(OH)(COOH)} + \underset{\text{Water.}}{H_2O.}$$

(2.) *From the monochlorinated or monobrominated acids of the acetic series.* By the action of argentic hydrate.

$$\underset{\text{Chloropropionic acid}}{C_2H_4Cl(COOH)} + \underset{\text{Argentic hydrate}}{AgHO} = \underset{\text{Lactic acid}}{C_2H_4(OH)(COOH)} + \underset{\text{Argentic chloride.}}{AgCl.}$$

(3.) *From the amidated derivatives of the acids of the acetic series.* By the action of nitrous acid.

$$\underset{\text{Amidoacetic acid}}{CH_2(NH_2)(COOH)} + \underset{\text{Nitrous acid}}{HNO_2} = \underset{\text{Glycollic acid}}{CH_2(OH)(COOH)} + \underset{\text{Water}}{H_2O} + \underset{\text{Nitrogen.}}{N_2.}$$

(4.) *From the ketones and aldehydes of the acetic series.* By first digesting these bodies with hydrocyanic acid, and acting on the resulting cyanides with dilute hydrochloric acid.

(5.) *The acids may be prepared as potassium salts*, by the action of a solution of potassic hydrate on the cyanides, or on the acid chlorides of the monochlorinated acids of the acetic series.

(6.) *They may be prepared as ethylic salts of the secondary acids*, by the action of the zinc organo-metallic compounds on ethylic oxalate and the subsequent addition of water.

$$(\alpha.)\ \left\{\begin{matrix}CO.OC_2H_5\\ CO.OC_2H_5\end{matrix}\right. + 2Zn(C_nH_{2n+1}) = \left\{\begin{matrix}C(C_nH_{2n+4})_2(OZnC_nH_{2n+1})\\ CO.O\ C_2H_5\end{matrix}\right. + Zn\left\{\begin{matrix}C_nH_{2n+1}\\ OC_nH_{2n+1}\end{matrix}\right.$$

Ethylic oxalate + Zinc compound.

$$(\beta.)\ \left\{\begin{matrix}C(C_nH_{2n+1})_2(OZnC_nH_{2n+1})\\ CO.OC_2H_5\end{matrix}\right. + 2H_2O = \left\{\begin{matrix}C(C_nH_{2n+1})_2(OH)\\ CO.OC_2H_5\end{matrix}\right. + Zn(OH)_2 + C_nH_{2n+2}$$

Secondary acid.

Properties (*General*).—All the acids of the lactic series furnish *metallic salts* by their action on metallic carbonates; *ethereal salts*, by their action on alcohols; *acid chlorides*, by their action on phosphoric chloride; *acids of the acetic series*, by their action on hydriodic acid; and either *anhydrides* or *acids of the acrylic series*, by the action of heat.

Carbonic Acid; $CO(OH)_2 = H_2CO_3$. The constitution of this acid allies it to the lactic series, but unlike the other acids of the series it is *dibasic*.

We need only note here that it forms:—

(*α*.) *Ethereal Salts*, such as, *e.g.*, ethylic carbonate $(C_2H_5)_2CO_3$. This is prepared by the action of argentic carbonate on ethylic iodide ($Ag_2CO_3 + 2C_2H_5I = 2AgI + (C_2H_5)_2CO_3$). Ethylic carbonate is a colorless liquid, boiling at 257° F. (125° C.). Derivatives of this ether are known where the oxygen is wholly or partially replaced by sulphur, as, *e.g.*—

Ethylic monosulphocarbonic acid	$(C_2H_5)H.CO_2S$.
Ethylic disulphocarbonic acid (*xanthic acid*)	$(C_2H_5)HCOS_2$.
Ethylic trisulphocarbonic acid	$(C_2H_5)HCS_3$.

(*β*.) *Amidogen Derivatives*, as, *e.g.*, *carbamic acid* $CO(NH_2)(OH)$, and *carbamide* (or *urea*) $CO(NH_2)_2$ from which latter body many compound ureas may be formed by the introduction of hydrocarbon groups in the place of hydrogen. When the oxygen, moreover, is replaced by sulphur, *sulpho-carbamide* or *sulpho-urea* ($CS(NH_2)_2$) is formed.

Glycollic Acid (*mono-oxy-acetic acid*) ($(CH_2OH)(COOH)=C_2H_4O_3$). *Molecular weight*, 76. *Melts at* 176° F. (80° C.). *Boils at* 212° F. (100° C.).

Preparation.—(1.) By the general processes already described (page 707).

(2.) By the action of nascent hydrogen on oxalic acid:—

$$\underset{\text{Oxalic acid}}{(COOH)(COOH)} + \underset{\text{Hydrogen}}{2H_2} = \underset{\text{Glycollic acid}}{(CH_2OH)(COOH)} + \underset{\text{Water.}}{H_2O.}$$

Properties.—These vary somewhat according to the preparation. A white crystalline solid, soluble in water, in alcohol, and in ether. Decomposed by a heat of 302° F. (150° C.). Yields oxalic acid by oxidation, and paramalic acid by dehydration.

Lactic Acid; $C_2H_4(OH)(COOH) = C_3H_6O_3$. There are at least two, and possibly more modifications of this acid.

(*α*.) *Ordinary lactic acid* ($CH_3.CH(OH)(COOH)$). This acid is produced (1) by the lactic acid fermentation; (2) by the oxidation of propene glycol; (3) by the action of argentic hydrate on chloropropionic acid; (4) by the action of nascent hydrogen on pyruvic acid; and (5) by the action of hydrocyanic acid on acetic aldehyde, and the subsequent digestion of the cyanide formed with hydrochloric acid.

(β.) *Paralactic* or *ethylene lactic acid*, $CH_2(OH)CH_2.(COOH)$. This is prepared by decomposing paralactyl chloride (formed by combining ethene with carbonyl chloride) with an alkali. It may also be obtained from the gastric juice, from the saliva of diabetic patients, from various secretions, and also from muscle (*sarcolactic acid*), by the action of cold water or of dilute alcohol.

Properties.—Lactic acid has never been obtained in the solid state, but its solution may be concentrated to a thick, colorless, syrupy liquid, having a specific gravity of 1·215. It is very acid and very soluble in water, alcohol, and ether. By the action of continuous heat, *lactide*, or *lactic anhydride* ($C_3H_4O_2$) is formed. This body is a white crystalline substance, melting at 256·1° F. (124·5° C.), combining with water to form *lactic acid*, and with ammonia to form *lactamide* ($C_2H_4(OH)CO(NH_2)$).

Heated with *dilute sulphuric acid*, lactic acid forms aldehyde and formic acid ; heated with *hydriodic acid*, it is reduced to propionic acid ($C_3H_6O_3 + 2HI = C_3H_6O_2 + H_2O + I_2$) : by *oxidation*, it yields acetic acid, formic acid, and carbonic anhydride ; by the action of *phosphoric chloride*, it forms chloro-propionic chloride ($C_2H_4ClCOCl$). All the lactates are soluble.

Lactic acid may be known from glycollic acid by its yielding no precipitate with plumbic acetate.

Paralactic acid yields by oxidation malonic acid. Varieties of this acid are said to have different actions on a polarized beam of light.

Pyruvic Series.

SERIES I. (β.)—*Formula* $C_nH_{2n-1}O(COOH)$.

The acids of this series are monobasic and dihydric. They may be regarded as derivatives of the lactic acid series by the abstraction of H_2. Thus—

$C_nH_{2n}(OH)(COOH)$; Acid of lactic series ; $C_nH_{2n-1}O(COOH)$. Acid of pyruvic series.

It includes :—

Name.	Formulæ.	Molecular Wt.	Remarks.
Glyoxalic acid	$C_2H_2O_3$	74	
Pyruvic acid .. .. (Pyroracemic acid)	$C_3H_4O_3$	88	A liquid prepared by the dry distillation of tartaric, glyceric or racemic acids. Boils at 329° F. (165° C.). With sodium amalgam or with HI (*i.e.* by nascent hydrogen) it forms lactic acid.

Glyoxylic Series.

SERIES I. (γ.)—*Formula* $C_nH_{2n-1}(OH)_2CO.OH$.

The acids of this series are monobasic and trihydric. They are derivatives of triatomic alcohols. Thus—

$$\underset{\text{Glycerin}}{C_3H_8O_3} \quad — \quad \underset{\text{Glyceric acid.}}{C_3H_6O_4.}$$

It includes :—

Name.	Formulæ.	Molecular Wt.	Remarks.
Glyoxylic acid .. (Dioxyacetic acid)	$CH(OH)_2(COOH)=C_2H_4O_4$	92	Prepared by the oxidation of glycol and of alcohol, and by the action of nascent hydrogen on oxalic acid. A colorless syrup; distils at 212° F. (100° C.) without change. Dissolves zinc without the evolution of hydrogen.
Glyceric acid .. (Dioxypropionic acid)	$CH_2(OH).CH(OH).(COOH)$ $=C_3H_6O_4$	106	Prepared by the action of nitric acid on glycerine, and by the spontaneous decomposition of nitro-glycerin. A thick syrup, forming iodopropionic acid ($C_3H_5IO_2$), when the product formed with phosphorus iodide is treated with water.

Acrylic Series.

SERIES II.—*Formula* $C_nH_{2n-1}(COOH)$.

The acrylic series of acids are mostly oily liquids, the primary acids existing as glycerides in natural fats and oils. They are monobasic, that is their salts are formed by the substitution of one equivalent of a metal for one of hydrogen. Fused with potassic hydrate, they eliminate hydrogen and form potassic acetate and a potassic salt of another acid—

$$\underset{\text{Oleic acid}}{C_{18}H_{34}O_2} + \underset{\text{Potassic hydrate}}{2KHO} = \underset{\text{Potassic acetate}}{C_2H_3KO_2} + \underset{\text{Potassic palmitate}}{C_{16}H_{31}KO_2} + \underset{\text{Hydrogen.}}{H_2.}$$

Nascent hydrogen converts them into the acids of the acetic series.

This series includes :—

Name.	Formulæ.	Remarks.
Acrylic acid	$C_2H_3(COOH)$	*Preparation.*—By the oxidation of acrolein, C_3H_4O. A colorless liquid freezing at 44·6° F. (7° C.), and boiling at 284° F. (140° C.). By the action of nascent hydrogen, it is converted into propionic acid ($C_3H_6O_2$), and by the action of bromine into dibromopropionic acid.
Crotonic acid.. ..	$C_3H_5(COOH)$	It was supposed to be the acid obtained by the saponification of croton oil, but this is doubtful. It is prepared by the oxidation of crotonic aldehyde. It is a white crystalline body melting at 161·6° F. (72° C.), and boiling at 357·8° F. (181° C.), evolving hydrogen when heated with potassic hydrate. There are three modifications of this acid.
Angelic Acid.. ..	$C_4H_7(COOH)$	Found in angelica or sumbul root, and also prepared by heating oil of camomile (angelic aldehyde) with potassic hydrate. A crystalline solid, melting at 113° F. (45° C.), and boiling at 374° F. (190° C.).
Pyroterebic acid ..	$C_5H_9(COOH)$	A liquid boiling at 410° F. (210° C.) prepared by the distillation of terebic acid.
Damaluric acid .. Damolic acid.. ..	$C_7H_{12}O_2$ $C_{12}H_{24}O_2$	Acids existing in the urine of cows and horses.
Moringic acid	$C_{15}H_{28}O_2$	Present in the oil of ben, together with stearic acid, etc.
Cimicic acid ..		A yellow crystalline acid extracted from a kind of bug.
Physetoleic acid ..	$C_{16}H_{30}O_2$	A crystalline acid obtained from sperm oil. It melts at 86° F. (30° C.).
Hypogæic acid ..	$C_{16}H_{30}O_2$	Exists as a glyceride in earth-nuts, with palmitic acid, etc. It melts at 93·2° F.(34° C.)
Gaïdic acid	$C_{16}H_{30}O_2$	Colorless crystals, melting at 100·4° F.(38° C.), prepared by the action of nitrous acid on hypogæic acid.
Oleic acid	$C_{18}H_{34}O_2$	An acid present as a glyceride (olein) in most natural fats and non-drying oils (*see* Candles). Crystallizes in white needles, which melt at 57·2° F. (14° C.). Specific gravity at 66·2° F. (19° C.) 0·898. Insoluble in water; soluble in alcohol, ether, and in sulphuric acid. Nitric acid converts it into acids of the acetic series, and nitrous acid converts it into elaidic acid. The solid acid is oxidized slowly, and the liquid acid rapidly, by exposure to air. Fused with potassic hydrate it yields acetate and palmitate of potassium.
Elaidic acid	$C_{18}H_{34}O_2$	By the action of nitrous acid on oleic acid. A crystalline body melting at 111·2°F.(44°C.).
Doeglic acid	$C_{19}H_{36}O_2$	An acid prepared from the oil obtained from the doegling or bottle-nose whale.
Brassic acid	$C_{22}H_{42}O_2$	An acid obtained from the oil of a species of brassica (colza).
Erucic acid	$C_{22}H_{42}O_2$	An acid from the oil of the black mustard.
Secondary Acids.		
Methacrylic acid ..	$C_3H_5(COOH)$	An acid isomeric with crotonic acid. A colorless oily liquid, prepared by the action of phosphorous chloride on ethylic dimethoxylate. Fused with potash, it yields hydrogen and potassic propionate and formate.
Methylcrotonic acid	$C_4H_7(COOH)$	
Ethylcrotonic acid	$C_5H_9(COOH)$	

Sorbic Series.

SERIES III.—*Formula* $C_nH_{2n-3}(COOH)$.

This includes :—

Name.	Formulæ.	Molecular Weight.	Fusing Point.		Occurrence and Preparation.
			° F.	° C.	
Tetroleic acid ..	$C_3H_3(COOH) = C_4H_4O_2$	84	168·8	76·0	Prepared by the action of potassic hydrate on chloro-crotonic acid.
Sorbic acid ..	$C_5H_7(COOH) = C_6H_8O_2$	112	273·2	134·0	Found in mountain-ash berries.
Palmitolic acid ..	$C_{15}H_{27}(COOH) = C_{16}H_{28}O_2$				
Stearolic acid ..	$C_{17}H_{31}(COOH) = C_{18}H_{32}O_2$	280	118·4	48·0	Prepared by the action of potassic hydrate on bromoleic acid.

Benzoic Series.

SERIES IV.—*Formula* $C_nH_{2n-7}(COOH)$.

Preparation.—(1.) By the oxidation of the corresponding aldehydes and alcohols. Thus benzoic acid may be obtained either from benzoic aldehyde ($C_6H_5.CHO$), or from benzylic alcohol ($C_6H_5.CH_2OH$).

(2.) By the action of alkalies on the nitriles (abnormal cyanides):—

C_6H_5CN	+	KHO	+	H_2O	=	$C_6H_5CO(OK)$	+	NH_3
Benzonitrile	+	Potassic hydrate	+	Water	=	Potassic benzoate	+	Ammonia.

(3.) By the action of water on the corresponding acid chlorides.

(4.) By the action of sodium and carbonic anhydride on the monobrominated derivatives of the C_nH_{2n-6} series of hydrocarbons—

C_6H_5Br	+	Na_2	+	CO_2	=	$C_6H_5CO(ONa)$	+	$NaBr$.
Bromobenzene	+	Sodium	+	Carbonic anhydride	=	Sodic benzoate	+	Sodic bromide.

This series includes :—

Name.	Formulæ.	Mol. Wt.	Melting Pt.		Boiling Pt.		
			° F.	° C.	° F.	° C.	
Benzoic acid ..	$C_6H_5CO(OH)$ $=C_7H_6O_2$	122	250·5	121·4	462·2	239·0	
Toluic acid ..	$C_6H_3(CH_3)CO(OH)$ $=C_8H_8O_2$	136	347·0	175·0			Exists in three modifications: (1.) *Paratoluic.* (2.) *Metatoluic.* (3.) *Orthotoluic.* A crystalline body with similar reactions to benzoic acid.
Alphatoluic acid	$C_6H_5CH_2CO(OH)$ $=C_8H_8O_2$	136	169·7	76·5	509·0	265·0	Prepared by General Process 2. A crystalline body.
Xylic acid .. (Xylilic acid)	$C_6H_3(SH_3)_2CO(OH)$ $=C_9H_{10}O_2$	150	248·0	120·0	523·4	273·0	Exists in two forms, as xylic and paraxylic acids.
Alphaxylic acid	$C_6H_4\begin{cases}CH_3\\CH_2CO(OH)\end{cases}$ $=C_9H_{10}O_2$	150	107·6	42·0			
Cumic acid ..	$C_6H_4(C_3H_7)CO(OH)$ $=C_{10}H_{12}O_2$	164	197·6	92·0			

Benzoic Acid ($C_6H_5CO.OH$).

Benzoic acid is present to about 15 per cent. in Gum Benzoin. It also occurs in Balsam of Peru and in some essential oils, such as cinnamon.

Preparation.—(α.) See General methods.

(β.) By the oxidation of a mixture of benzene and formic acid.

(γ.) From Gum Benzoin (in which it exists ready formed) by sublimation.

(δ.) By the action of hydro-chloric acid on hippuric acid, fermented urine of horses or cows. (This process is employed in its preparation on a large scale.)

Properties.—Feathery crystals soluble in alcohol and in boiling water.

Reactions.—Decomposed at a red heat into carbonic acid and benzene. Forms substitution products with chlorine, bromine, and iodine, also with nitric and sulphuric acids. With nascent hydrogen it forms hydrobenzoic acid (C_6H_9COOH).

All the benzoates are soluble, and are easily formed directly or by double decomposition.

Some of the derivatives of benzoic acid need further notice.

Benzoic Chloride; *Benzoyl chloride* (C_7H_5OCl).

Preparation.—By the action of phosphorus pentachloride on benzoic acid.

Properties.—A colorless, pungent liquid. Specific gravity, 1·106. Its vapor is heavy, and burns with a greenish flame.

Benzoic Anhydride or **Oxide** ($C_{14}H_{10}O_3$).

Preparation.—By the action of benzoyl chloride on potassic benzoate ($C_7H_5O(ONa) + C_7H_5OCl = (C_7H_5O)_2O + NaCl$).

Properties.—It forms oblique rhombic prisms, melting at 42° C. .

Benzoic peroxide ($C_{14}H_{10}O_4$).

Chlorobenzoic Acid, $C_6H_4Cl.(COOH)$.

Preparation.—By the action of potassic chlorate and hydrochloric acid on benzoic acid.

Bromobenzoic Acid, $C_6H_4Br(COOH)$.

Preparation.—By the action of bromine on argentic benzoate.

Nitrobenzoic Acid, $C_6H_4(NO_2)(COOH)$.

Preparation.—By boiling benzoic acid in fuming nitric acid.

Properties.—A crystalline substance.

Hippuric or **Benzamidacetic Acid** ($C_9H_9NO_3$) = ($C_6H_5CONH CH_2COOH$).

Natural History.—Hippuric acid occurs as a potassium and sodium salt in the urine of horses, cows, etc., and also in human urine, more especially after the administration of benzoic acid.

In preparing the acid from urine it is necessary that it should be fresh, otherwise it evolves ammonia, benzoic acid being formed by the action of heat on the hippuric acid.

Preparation.—By the action of the zinc salt of amidacetic acid on benzoic chloride.

Properties.—The acid crystallizes in slender prisms. It melts when heated, and at a high temperature is decomposed, forming benzoic acid, benzonitrile, etc. It is slightly soluble in water (1 in 400 at 60° F.), and in hot alcohol.

Its reaction is acid. With hot sulphuric acid, it yields benzoic acid; with hot hydrochloric acid, amidacetic acid and benzoic acid; with nitric acid, benzoglycollic acid with the evolution of nitrogen.

It is monobasic, and forms salts called hippurates.

Oxybenzoic or Salicylic Series.

SERIES IV. (*a.*)—*Formula* $C_nH_{2n-8}(OH)COOH$.

The acids of this series are monobasic and dihydric. They are related to benzoic acid in the same manner as the lactic series is related to the acetic series.

It includes :—

Name.	Formulæ.	Preparation and Properties.
Salicylic acid (orthoxybenzoic acid)	$C_6H_4(OH)(COOH)$ $=C_7H_6O_3$	*Preparation.*—(1.) By passing CO_2 into phenol containing small pieces of sodium. (2.) By melting salicin or coumaric acid with potassic hydrate ($C_7H_6O_2+KHO=C_7H_5KO_3+H_2$). (3.) By distilling oil of wintergreen with potash. *Properties.*—A crystalline body, melting at 368·6° F. (187° C.), decomposed at 428° F. (220° C.), evolving phenol. Dissolves in cold water (1 in 1,000). With PCl_5 it forms chlorobenzoic chloride. Its solution gives a violet color to ferric salts.
Oxybenzoic acid (metoxybenzoic acid)	$C_6H_4(OH)(COOH)$ $=C_7H_6O_3$	*Preparation.*—By the action of nitrous acid on amido-benzoic acid. *Properties.*—A crystalline body, melting at 390·2° F. (199° C.) Requires a high temperature to decompose it. It gives no violet color with ferric salts.
Paraoxybenzoic acid ..	$C_6H_4(OH)(COOH)$ $=C_7H_6O_3$	Prepared by heating anisic acid with HI. Soluble in water (1 in 126 at 60° F.) Melts at 410° F. (210° C.) With ferric salts gives a yellow precipitate.
Anisic acid	$C_8H_8O_3$	Prepared by oxidising anisic aldehyde ($C_8H_8O_2$) or crude oil of aniseed. Colorless crystals, melting at 347° F. (175° C.). Soluble in alcohol, ether, and hot water.
Cresotic acid (carbocresylic acid)	$C_6H_3(OH)\left\{\begin{array}{l}CH_3\\(COOH)\end{array}\right.$	Prepared by the action of CO_2 and Na on cresol (C_7H_8O). *Orthocresotic acid* melts at 237·2° F. (114° C.); *paracresotic acid* at 298·4° F. (148° C.), and *metacresotic acid* at 338° F. (170° C.). They all produce a deep violet color with ferric chloride.
Oxymethylbenzoic acid.	$C_6H_4\left\{\begin{array}{l}(CH_2OH)\\(COOH)\end{array}\right.$	
Mandelic acid (formobenzoic)	$CH(OH)\left\{\begin{array}{l}C_6H_5\\(COOH)\end{array}\right.$	Prepared by the action of HCl on bitter almond oil.
Phloretic acid .. .. Hydrocoumaric acid .. Hydroparacoumaric acid	$C_2H_4\left\{\begin{array}{l}C_6H_4(OH)\\(COOH)\end{array}\right.$	Melts at 264·2° F. (129° C.) Prepared by the action of potash on phloretin. *Phloretic acid* gives a *green* color with ferric chloride, whilst *isophloretic acid* has no action.
Phenyllactic acid.. ..	$C_2H_3(OH)\left\{\begin{array}{l}C_6H_5\\(COOH)\end{array}\right.$	
Thymylcarbonic acid or thymotic acid	$C_6H_2(OH)\left\{\begin{array}{l}C_3H_7\\CH_3\\(COOH)\end{array}\right.$	*Preparation.*—By the action of CO_2 and Na on thymol. It melts at 248° F. (120° C.), and gives a blue color with ferric chloride.

Dioxybenzoic Series.

SERIES IV. (β.)—*Formula* $C_nH_{2n-9}(OH)_2(COOH)$.

These are monobasic acids, and include :—

Name.	Formulæ.	Preparation and Properties.
Pyrocatechuic acid .. Carbo-hydroquinonic acid.		Prepared by melting potash either with piperic or quinic acid, or with kino, catechu, etc. When the acid is heated, it yields CO_2 and pyrocatechin.
Oxysalicylic acid ..	$C_6H_3(OH)_2CO(OH)$	By the action of potash on iodo-salicylic acid. It melts at 379·4° F. (193° C.), and is decomposed at 418·6° F. (212° C.), yielding anthrachrysone. It is soluble in water, alcohol, and ether. It strikes a deep blue with ferric chloride.
Dioxybenzoic acid ..	$C_6H_3(OH)_2CO(OH)$	

Gallic Series.

SERIES IV. (γ.)—*Formula* $C_nH_{2n-10}(OH)_3(COOH)$.

Gallic Acid (*Trioxybenzoic acid*), $C_6H_2(OH)_3CO(OH) = C_7H_6O_5$. *Molecular weight*, 170.

Natural History.—It is found in gall nuts, acorns, hellebore root, black and green tea, etc.

Preparation.—By the action of argentic hydrate on di-iodo-salicylic acid.

Properties.—(*a.*) *Physical.* A white crystalline body ($C_7H_6O_5.OH_2$) having a powerful astringent taste. At 419° F. (215° C.) it is decomposed into CO_2 and pyrogallic acid ($C_6H_6O_3$), whilst by a heat of 480·2° F. (249° C.) it is resolved into carbonic anhydride, water and metagallic acid ($C_6H_2O_2$). It is soluble in water (1 in 100 at 60° F., and 1 in 3 at 212° F.).

(*β.*) *Chemical.*—The solution has an acid reaction and rapidly decomposes. It does not precipitate gelatine. It forms a black precipitate with iron salts, the color disappearing by heat in the case of ferric salts, but not in the case of ferrous salts. It is readily oxidized, and hence rapidly reduces gold and silver salts. When boiled with a solution of arsenic acid, tannic acid is formed.

(For the TANNINS *see* SUPPLEMENTARY CHAPTER.)

Cinnamic Series.

SERIES V.—*Formula* $C_nH_{2n-9}(COOH)$.

This series is monobasic. The cinnamic series is related to the benzoic series in a similar manner as the acrylic is related to the acetic series of acids. Thus :—

$$C_nH_{2n+1}(COOH) \quad — \quad C_nH_{2n-1}(COOH);$$

Acetic — Acrylic.

$$C_nH_{2n-7}(COOH) \quad — \quad C_nH_{2n-9}(COOH)$$

Benzoic — Cinnamic.

It includes :—

Acids.	Formulæ.	Molecular Weight.	Melting Point.		
			° F.	° C.	
Cinnamic	$C_8H_7(COOH)$	148	248·0	120·0	*Preparation.*—(1.) By heating benzoic aldehyde with acetic chloride ($C_7H_6O + C_2H_3OCl = HCl + C_9H_8O_2$). (2.) By the oxidation of cinnamon oil. It is present ready formed in the balsams of Peru and Tolu. *Properties.*—A crystalline body, boiling at 559·4° F. (293° C.). Soluble in alcohol, not very soluble in water. With *nitric* or with *chromic acid* it forms benzoic acid and benzoic aldehyde. With *nascent hydrogen* (water and sodium amalgam), or heated with *hydriodic acid*, it forms hydrocinnamic acid ($C_9H_{10}O_2$). Fused with *potassic hydrate* it forms potassic benzoate and acetate. By *heat* it forms CO_2 and cinnamene (C_8H_8).
Atropic	$C_8H_7(COOH)$	148	222·8	106·0	Formed together with tropine ($C_8H_{15}(NO)$) from atropine, by the action of alkalies.
Isatropic	$C_8H_7(COOH)$	148	392·0	200·0	

SERIES V. (*a.*)—*Formula* $C_nH_{2n-11}(COOH)$.

This includes phenyl-propiolic acid, $C_6H_5C_2CO(OH)$, a crystalline acid melting at 276·8° F. (136° C.). It is prepared by the action of potassic hydrate on bromocinnamic acid, and is converted by nascent hydrogen into hydrocinnamic acid.

Naphtoic Series.

SERIES VI.—*Formula* $C_nH_{3n-13}(COOH)$.

This series includes two isomeric acids, *viz.*, α-naphtoic acid, and β-naphtoic acid. The former melts at 320° F. (160° C.), and the latter at 359·6° F. (182° C.). By the action of sodium and carbonic anhydride on α- and β-naphtol, the two isomeric acids α- and β-oxy-naphtoic acids are formed.

SERIES VI.—(*a.*) *Formula* $C_nH_{2n-19}(COOH)$.

This includes *anthracene carboxylic acid*, $C_{14}H_9(COOH)$, a solid body, melting at 402·8° F. (206° C.). It is prepared by heating anthracene with carbonic oxychloride. When heated it yields anthracene and carbonic anhydride.

B. DIBASIC ACIDS.

That is, acids containing two semi-molecules of carboxyl (COOH).

Succinic Series.

SERIES I.—*Formula* $C_nH_{2n}(COOH)_2$.

Preparation (*General*).—(1.) By the oxidation of many fatty organic bodies, such as suet, etc., with nitric acid.

$$\begin{array}{ccccccccc} C_4H_8O_2 & + & O_3 & = & H_2O & + & C_4H_6O_4. \\ \text{Butyric acid} & + & \text{Oxygen} & = & \text{Water} & + & \text{Succinic acid.} \end{array}$$

(2.) By the oxidation of the primary glycols.

$$\begin{array}{ccccccc} C_2H_4(OH)_2 & + & 2O_2 & = & 2H_2O & + & C_2O_2(OH)_2. \\ \text{Glycol} & + & \text{Oxygen} & = & \text{Water} & + & \text{Oxalic acid.} \end{array}$$

(3.) By the action of potassic hydrate or hydrochloric acid on the nitriles (cyanides) of the dyad radicals.

$$\left\{\begin{array}{l} C_nH_{2n}(CN) \\ C_nH_{2n}(CN) \end{array}\right. + 2KHO + 2H_2O = \left\{\begin{array}{l} C_nH_{2n}(COKO) \\ C_nH_{2n}(COKO) \end{array}\right. + 2NH_3$$

(4.) By the action of sodium or silver on the iodo-derivatives of the acetic acid series. Thus:—

$$2C_nH_{2n}I(COOH) + Ag_2 = C_{2n}H_{4n}(COOH)_2 + 2AgI.$$

Properties (*General*).—These dibasic acids are all crystalline solids yielding by heat either the anhydride and water, or carbonic anhydride and an acid of the acetic series.

Thus it will be noted that the acids of the succinic series are related (α) to the *glycols*, as seen by the second method of preparation described above; (β) to the *dyad radicals*, as seen by the third method, and by the further fact that in some cases they yield the hydride of the radical, when heated with an excess of caustic baryta; and (γ) to the *acids of the acetic series*, as seen by the fourth method of preparation. Conversely moreover, in some cases, the succinic series may be converted into the acetic, by the abstraction of carbonic anhydride.

This series includes—

Name.	Formulæ.	Molecular Weight.	Melting Pt.		Boiling Pt.		Remarks.
			° F.	° C.	° F.	° C.	
Oxalic	$(COOH)_2$	90					See below.
Malonic .	$CH_2(COOH)_2$	104	284·0	140			Prepared by the oxidation of malic acid and of propene glycol. Decomposed at 302° F. (150° C.).
Succinic ..	$C_2H_4(COOH)_2$	128	356·0	180	455	235	See page 720.
Pyrotartaric	$C_3H_6(COOH)_2$	132	233·6	112			Prepared by heating tartaric acid. It volatilizes at 392° F. (200° C.).
Adipic	$C_4H_8(COOH)_2$	146	284·0	140	}		By the oxidation of fats with nitric acid.
Pimelic ..	$C_5H_{10}(COOH)_2$	160	273·2	134			Prepared by the oxidation of cork with nitric acid, and by the action of nitric acid on certain fats. Fusible and volatile.
Suberic ..	$C_6H_{12}(COOH)_2$	174	257·0	125			
Anchoic .. (Separgylic)	$C_7H_{14}(COOH)_2$	188	240·8	116			By the action of nitric acid on Chinese wax, and on the fatty acids of cocoa-nut oil.
Sebacic ..	$C_8H_{16}(COOH)_2$	202	260·6	127			Prepared by the destructive distillation of oleic acid.
Rocellic ..	$C_{15}H_{30}(COOH)_2$	300	269·6	132			Present in certain lichens. Volatile at 392° F. (200° C.).

Oxalic Acid.—$(COOH)_2 = C_2H_2O_4$; (crystals $= C_2H_2O_4,2H_2O$).

Natural History.—Oxalic acid is present in most plants, either in a free state, or as a lime or alkaline oxalate (potassic oxalate in common sorrel, calcium oxalate in rhubarb). It occurs very frequently as a lime-salt in the urine (mulberry calculus). Its formation in this latter case is no doubt due to some imperfection in the normal oxidizing process going on in the body, the carbon and hydrogen not being converted, as usual, into water and carbonic anhydride.

Preparation.—(1.) By the oxidation of organic compounds, such as sawdust, sugar, etc., either by the action of nitric acid, or by their fusion with potassic hydrate, whereby a potassic oxalate is formed.

$$\underset{\text{Sugar}}{C_{12}H_{22}O_{11}} + \underset{\text{Oxygen}}{O_{18}} = \underset{\text{Oxalic acid}}{6C_2H_2O_4} + \underset{\text{Water.}}{5H_2O.}$$

(2.) By the direct combination of an alkaline metal with carbonic anhydride.

$$\underset{\text{Carbonic anhydride}}{2CO_2} + \underset{\text{Sodium}}{Na_2} = \underset{\text{Sodic oxalate.}}{Na_2C_2O_4.}$$

(3.) By the decomposition of cyanogen with water.

$$\underset{\text{Cyanogen}}{C_2N_2} + \underset{\text{Water}}{4H_2O} = \underset{\text{Oxalic acid}}{C_2H_2O_4} + \underset{\text{Ammonia.}}{2NH_3.}$$

(4.) By the action of heat on potassic formate ($2HCO(OK) = H_2 + K_2C_2O_4$).

(5.) By the oxidation of ethylene glycol (see page 718).

Commercial preparation of Oxalic Acid.—A thick paste is first prepared by mixing sawdust with a solution containing potassic hydrate (1 equiv.) and sodic hydrate (2 equiv.), the alkaline solution having a specific gravity of 1·35. This paste is then heated on iron plates at 400° F. (204° C.) for some hours, whereby hydrogen is evolved from the decomposition of the water of the alkaline hydrates, whilst the oxygen liberated oxidizes the sawdust. The grey mass formed contains about one-fourth its weight of oxalic acid. This is then treated with water, which leaves the oxalate of soda undissolved, owing to its insolubility in water. The insoluble residue, after the action of the water, is then boiled with lime, and the resulting calcic oxalate decomposed with sulphuric acid. The clear liquor containing the oxalic acid is then evaporated down and crystallized.

The sawdust yields on an average about half its weight of crystallized oxalic acid.

The alkalies are recovered from the liquid with which the mass is first treated by evaporating the solution to dryness, calcining the residue, in order to destroy any organic matter present, and afterwards decomposing the carbonates with calcic hydrate. The recovered alkalies may then be used for a new operation.

Properties.—(*a.*) *Physical.* Oxalic acid consists of colorless crystals (oblique rhombs). At a heat of 212° F. (100°C.) the water of crystallisation is driven off. At 320° F. (160° C.) the acid sublimes, but at a temperature above this it is decomposed into formic acid and carbonic anhydride ($C_2H_2O_4=CH_2O_2+CO_2$), the formic acid being afterwards further decomposed by heat into water and carbonic oxide ($CH_2O_2=CO+H_2O$). It is soluble in water (1 in 8 at 60° F., and 1 in 1 at 212° F.), and also in alcohol. The acid is poisonous. Chalk and magnesia constitute the proper antidotes.

(β.) *Chemical.* The solution of oxalic acid is very acid to litmus. *Sulphuric acid* converts it into H_2O,CO_2 and CO. *Nitric acid* acts slowly upon it, converting it into CO_2. Heated with *alkalies*, it yields hydrogen and an alkaline carbonate.

Uses.—In calico-printing; in cleansing brass and leather; also as a solvent for Prussian blue in the manufacture of blue ink.

It forms salts called oxalates, a few of which we note as follows:—

Name.	Formulæ.	Solubility in water.		Remarks.
		50° F.	212° F.	
Potassium oxalates. Neutral	$C_2K_2O_4 2aq$	1 in 3		
Acid (binoxalate or salt of sorrel) ..	$C_2HKO_4 2aq$	1 in 40	1 in 6	
Hyperacid or quadroxalate	$C_2HKO_4,C_2H_2O_4,2aq$			
Sodic oxalate..		almost	insoluble	
Ammonium oxalates. Neutral	$C_2(NH_4)_2O_4 2aq$	not very soluble	very soluble	Yields by heat oxamide; heated with phosphoric anhydride it forms cyanogen.
Acid (binoxalate) ..	$C_2H(NH_4)O_4 aq$			Yields oxamic acid by heat.
Calcic oxalate	$C_2Ca''O_4 4aq$	insoluble		
Ferrous oxalate	$C_2Fe''O_4$	insoluble		
Ferric oxalate	$Fe_2(C_2O_4)_3 3aq$	very soluble		
Ethyl oxalate (oxalic ether)	$(C_2H_5)_2C_2O_4$			Sp. Gr. 1·09. Boils at 188·1° F. (84·3° C.).
Acid ethyl oxalate or ethyl-oxalic acid	$(C_2H_5)C_2HO_4$			

All the oxalates are decomposed by heat. The alkaline and the earthy oxalates, if not too strongly heated, evolve CO, and leave carbonates of the metals, whilst the oxalates of other metals leave metallic oxides. With sulphuric acid the oxalates break up into CO and CO_2, leaving a residue of sulphate, which residue, however, does not blacken by the action of the acid, inasmuch as no separation of carbon takes place.

Succinic Acid.—$C_2H_4(COOH)_2=C_4H_6O_4$. [*Molecular weight,* 128. *Fuses at* 356° F. (180° C.). *Boils at* 455° F. (235° C.)]

Natural History.—It is found in amber, in some lignites, and occasionally in animal and vegetable substances (lettuce, unripe grapes, urine of some animals, etc.).

Preparation.—(1.) By the action of potassic hydrate on ethylene cyanide—

$$\underset{\text{Ethylene cyanide}}{C_2H_4(CN)_2} \quad \underset{+}{+} \quad \underset{\text{Water}}{4H_2O} \quad \underset{=}{=} \quad \underset{\text{Ammonia}}{2NH_3} \quad \underset{+}{+} \quad \underset{\text{Succinic acid.}}{C_4H_6O_4.}$$

(2.) By the oxidation of butyric acid—

$$\begin{array}{ccccccc} C_4H_8O_2 & + & O_3 & = & H_2O & + & C_4H_6O_4. \\ \text{Butyric acid} & + & \text{Oxygen} & = & \text{Water} & + & \text{Succinic acid.} \end{array}$$

(3.) By the action on malic acid, either of (α) nascent hydrogen, or (β) fermentation, or (γ) hydriodic acid.

(α.) $C_4H_6O_5+H_2=H_2O+C_4H_6O_4$.

(γ.) $C_4H_6O_5+2HI=H_2O+I_2+C_4H_6O_4$.

Properties.—Colorless crystals (oblique rhombs). It melts at 356° F. (180° C.), and boils at 455° F. (235° C.), water and succinic anhydride ($C_4H_4O_3$) being formed. [*Iso-succinic acid* melts at 266° F. (130° C.), and boils at 302° F. (150° C.), forming CO_2 and propionic acid ($C_3H_6O_2$).]

It is soluble in water (1 in 5 at 60° F., 1 in 3 at 212° F.). With nascent oxygen it yields ethylene, CO_2, and H_2O; ($C_4H_6O_4+O=C_2H_4+2CO_2+H_2O$). Nitric and hydrochloric acids have no action upon it. Distilled with H_2SO_4 and MnO_2, it yields acetic acid.

Distinctive Reactions of Succinic Acid.—*Succinic acid* (as a sodic salt) gives a red-brown precipitate with ferric chloride. *Iso-succinic acid* gives none.

Succinic acid is not precipitated from its salts by the mineral acids. It gives a white precipitate with $BaCl_2$, on the addition of an alcoholic solution of ammonia. *Benzoic acid* is precipitated from its salts by the mineral acids. It gives no precipitate with $BaCl_2$.

Malic Series.

SERIES I. (*a*.)—*Formula* $C_nH_{2n-1}(OH)(CO.OH)_2$.

These acids are trihydric and dibasic:—

NAMES.	Formulæ.	Remarks.
Tartronic .. .. (oxymalonic).	$CH(OH)(COOH)_2 = C_3H_4O_5$	*Preparation.*—By the spontaneous decomposition of nitro-tartaric acid.
Malic .. .. .. (oxysuccinic).	$C_2H_3(OH)(COOH)_2 = C_4H_6O_5$	Malic acid is widely distributed in plants as in the juices of apples, pears, etc. (with citric acid), or of rhubarb (with acid potassic oxalate), or in the berries of the mountain ash, or in tobacco leaves (as bimalate of lime). *Preparation.*—(1.) From the above juices. (2.) By the action of nitrous acid on asparagine ($C_4H_8N_2O_3$) and on aspartic acid ($C_4H_7NO_4$), bodies found in the asparagus, the marsh mallow, etc. ($C_4H_8N_2O_3$ asparagine $+ 2HNO_2 = C_4H_6O_5 + 2H_2O + 2N_2$). (3.) By the action of argentic hydrate on monobromo-succinic acid. *Properties.*—Crystalline, soluble in water and in alcohol. With *ferments*, such as putrefying cheese, it yields CO_2, succinic and acetic acids; digested with *hydriodic acid* in sealed tubes, it yields succinic acid; fused with *potassic hydrate*, or boiled with a *strong mineral acid*, it yields sorbic acid.

Tartaric Series.

SERIES I. (β.)—*Formula* $C_nH_{2n-2}(OH)_2(COOH)_2$.

These acids are tetrahydric and dibasic :—

NAMES.	Formulæ.	Remarks.
Mesoxalic	$C(OH)_2(CO.OH)_2$	A uric acid derivative. By deoxidation it forms tartronic and afterwards malonic acid.
Tartaric .. .. (dioxysuccinic).	$C_2H_2(OH)_2(CO.OH)_2$	*See* below.

Tartaric Acid, $C_2H_2(OH)_2(CO.OH)_2=C_4H_6O_6$.—*Molecular Weight,* 150.

Natural History.—Ordinary tartaric acid constitutes the acid of grapes, and, together with citric, oxalic, and malic acids, is found in numerous plants.

Commercial Preparation.—(*a.*) *Argol* or *tartar* (*hydric potassic tartrate,* $KHC_4H_4O_6$), a substance deposited from fermenting grape juice, is first purified by solution in hot water, and subsequent crystallization (cream of tartar).

(*β.*) This purified residue is now dissolved in hot water and boiled with powdered chalk, whereby an *insoluble* calcic tartrate, and a *soluble* potassic tartrate are formed :

$$\begin{array}{ccccccccccccc} 2KHC_4H_4O_6 & + & CaCO_3 & = & K_2C_4H_3O_6 & + & Ca''C_4H_4O_6 & + & H_2O & + & CO_2. \\ \text{Hydric potassic tartrate} & + & \text{Calcic carbonate} & = & \text{Potassic tartrate} & + & \text{Calcic tartrate} & + & \text{Water} & + & \text{Carbonic anhydride.} \end{array}$$

(*γ.*) Calcic chloride is now added to the clear solution, whereby the whole of the tartaric acid is precipitated as calcic tartrate : thus,

$$\begin{array}{ccccccc} K_2C_4H_4O_6 & + & Ca''Cl_2 & = & 2KCl & + & Ca''C_4H_4O_6. \\ \text{Potassic tartrate} & + & \text{Calcic chloride} & = & \text{Potassic chloride} & + & \text{Calcic tartrate.} \end{array}$$

(*δ.*) This tartrate of lime is now collected and boiled with dilute sulphuric acid, whereby an insoluble calcic sulphate is formed, whilst the filtered solution contains the free tartaric acid :

$$\begin{array}{ccccccc} Ca''C_4H_4O_6 & + & H_2SO_4 & = & C_4H_6O_6 & + & C''SO_4. \\ \text{Calcic tartrate} & + & \text{Sulphuric acid} & = & \text{Tartaric acid} & + & \text{Calcic sulphate.} \end{array}$$

Tartaric acid may also be prepared by the action of nitric acid on gum or sugar of milk.

Varieties.—There are four modifications of tartaric acid :—

(*a.*) *Dextro-* or *common tartaric acid,* so called from its property of causing the plane of polarization to rotate to the right.

(*β.*) *Lævo-tartaric acid,* which rotates the plane of polarization to the left.

(*γ.*) *Inactive* or *meso-tartaric acid,* which is without action on a polarized ray. It, moreover, cannot be resolved into dextro- and lævo-tartaric acids. In this latter respect it differs from *paratartaric* or *racemic acid,* which is also without action on a polarized ray, but which is a compound of dextro- and lævo-tartaric acid, and is capable of resolution into these two modifications of the acid.

(δ.) *Metatartaric acid.* An uncrystallizable modification produced by fusing the ordinary acid.

Properties of common tartaric acid.—(α.) *Physical.* Colorless crystals (oblique rhombs), inodorous, having an acid taste, permanent in the air, and very soluble in water and alcohol. The crystals fuse at 340° F. (171·1° C.), forming metatartaric and isotartaric acids, both of which are uncrystallizable acids. At 374° F. (190° C.) it loses water, and becomes tartaric anhydride ($C_8H_8O_{10}$), which, by long boiling in water, may be converted into tartaric acid. At a temperature of 401° F. (205° C.) it forms paratartaric acid and CO_2.

(β.) *Chemical.*—Its solution is very acid, and rapidly decomposes by keeping, acetic acid being formed and a fungus deposited which contains 3·5 per cent. of nitrogen.

With *hydriodic acid,* it forms succinic and malic acids ; with *powerful oxidizing agents*, it forms formic acid ; with *less powerful oxidizing agents*, tartronic acid ; fused with *potassic hydrate*, it yields potassic oxalate and acetate, but no hydrogen is evolved ; with concentrated *sulphuric acid,* it is carbonized ; with *phosphorus pentachloride*, it forms chloromaleic chloride ; with *acetic chloride*, it forms diacetotartaric acid, $C_2H_2(OC_2H_3O)_2(COOH)_2$; and with *alcohols*, it forms the various ethereal salts.

The following represent the formulas of some of the tartrates :—

NAMES.		Formulæ.	Solubility in water.
Potassic tartrates	neutral ..	$K_2C_4H_4O_6$	Very soluble.
	acid (Cream of tartar) ..	$KHC_4H_4O_6$	Soluble in boiling but not in cold water.
Ammonic tartrates	neutral ..	$(NH_4)_2C_4H_4O_6$+aq.	Soluble.
	acid ..	$(NH_4)HC_4H_4O_6$	Do.
Sodic tartrates	neutral ..	$Na_2C_4H_4O_6$+2 aq.	Do.
	acid ..	$NaHC_4H_4O_6$+aq.	Do.
Rochelle salt or Seignette salt	Potassic and sodic tartrate	$KNaC_4H_4O_6$+4 aq.	1 in 1½ at 60° F. (15·5° C.)
Potassio-antimonious tartrate, or tartar emetic		$K(SbO)C_4H_4O_6$+aq. heated to 400° F. becomes $KSbC_4H_2O_6$.	1 in 15 at 60° F. (15·5° C.) 1 in 3 at 212° F. (100° C.)

Racemic Acid has the same composition as tartaric acid. It yields the same products as tartaric acid by heat, and forms analogous salts. It differs, however, from tartaric acid in being less soluble in water, and in its solution neither rotating the plane of polarization, nor precipitating a neutral calcic salt.

Fumaric Series.

SERIES II.—*Formula* $C_nH_{2n-2}(CO.OH)_2$.

These dibasic acids form succinic acid with nascent hydrogen, and substitution derivatives of succinic acid with the haloid acids and with the halogens. They also form monochlorinated acids of the malic series with hypochlorous acid.

The series include the following:—

ACIDS.	Formulæ.	Melting Pt.		Remarks.
		° F.	° C.	
Fumaric ..	$C_2H_2(COOH)_2$	About 392·0	200·0	The acid of the common fumitory. Prepared, together with maleic acid, by the action of heat on malic acid. It is a crystalline insoluble acid (1 in 200 at 60° F.). By heat it forms maleic anhydride. With nascent hydrogen it forms succinic acid.
Maleic	$C_2H_2(COOH)_2$	266·0	130·0	(See above for preparation). A crystalline, volatile soluble acid. Its reactions are similar to those of fumaric acid.
Citraconic ..	$C_3H_4(COOH)_2$	176·0	80·0	Prepared from citric acid. *Citraconic acid* is formed by the prolonged action of heat on citric acid. It is very soluble in water. *Itaconic acid* results when citraconic acid is heated with water for some hours. It is not very soluble in water. *Mesaconic acid* is formed by decomposing the product of the action of heat on a mixture of citraconic and hydrochloric acids. With nascent hydrogen, all three yield pyrotartaric acid. The three acids when treated with bromine yield three isomeric brominated acids.
Itaconic ..		320·0	160·0	
Mesaconic ..		392·9	200·5	

Phthalic Series.

SERIES III.—*Formula* $C_nH_{2n-8}(CO.OH)_2$.

These include—

ACIDS.	Formulæ.	Melting Point.		
		° F.	° C.	
Phthalic ..	$C_6H_4(CO.OH)_2$	365·0	185	By oxidizing benzene and formic acid by MnO_2 and H_2SO_4.
Isophthalic ..		Above 572	Above 300	
Terephthalic				

C.—TRIBASIC ACIDS,

and Acids of Higher Basicity, etc.

Tricarballylic Series.

SERIES I.—*Formula* $C_nH_{2n-1}(CO.OH)_3$.

Tricarballylic Acid, $C_3H_5(CO.OH)_3 = C_6H_8O_6$ is a trihydric acid, and is produced by the reduction of aconitic acid with sodium amalgam, or of citric acid with hydriodic acid.

$C_6H_8O_7$	+	$2HI$	=	$C_6H_8O_6$	+	H_2O	+	I_2.
Citric acid	+	Hydriodic acid	=	Tricarballylic acid	+	Water	+	Iodine.

Citric Acid (*oxytricarballylic acid*), $C_3H_4(OH)(COOH)_3 = C_6H_8O_7$.

Natural History.—This acid is found in the juice of lemons and oranges, and also in many fruits, such as gooseberries, etc., in conjunction with malic acid.

Preparation.—The lemon juice is first allowed to ferment, so that mucilage and other impurities may separate. The clear liquor is then neutralized with chalk, whereby an insoluble calcic citrate ($Ca_3 2C_6H_5O_7$) is formed. The precipitate is collected and decomposed with dilute sulphuric acid, the citric acid being afterwards crystallized from the solution.

Properties.—(*a*.) A crystalline dimorphous body, freely soluble in hot and cold water. The crystals fuse at 212° F. (100° C.), and decompose at 300° F. (149° C.), forming aconitic acid. Heated to 338° F. (170° C.), it forms itaconic acid.

(β.) *Chemical.*—A tribasic tetrahydric acid. The solution reddens litmus and rapidly decomposes.

It ferments *with putrid flesh,* forming butyric and succinic acids. *Sulphuric acid* decomposes it. *Nitric acid* converts it into oxalic acid. With *potassic hydrate,* it forms acetic and oxalic acids.

Citric, like tartaric acid, prevents the precipitation of ferric oxide by ammonia. The soluble compound formed has not been very well made out.

The acid is used in medicine, in dyeing, and in calico printing.

Desoxalic or **Trioxycarballylic Acid** ($C_3H_2(OH)_3(COOH)_3 = C_6H_8O_9$), is an unstable acid, and forms, when heated, tartaric and glyoxylic acid.

Meconic Acid ($C_7H_4O_7$) is a tribasic acid present in opium, and consists of mica-like plates, soluble in alcohol and in boiling water, but insoluble in cold water.

Mellitic Acid, $C_6(CO.OH)_6$, is a hexabasic acid, existing as an aluminic salt in "*honey stone.*"

We may note that, with one exception, the whole of the benzene

(C_6H_6) series of acids (*i.e.* acids derived by the substitution of the group COOH for the hydrogen of the benzene), are known. Thus—

Benzoic acid	C_6H_5COOH.
Phthalic acid, etc.	$C_6H_4(COOH)_2$.
Trimellitic acid, etc.	$C_6H_3(CO.OH)_3$.
Pyromellitic acid, etc.	$C_6H_2(COOH)_4$.
Unknown	$C_6H(CO.OH)_5$.
Mellitic acid	$C_6(COOH)_6$.

REACTIONS OF SOME OF THE CHIEF ACIDS.

(I.) Group reactions. (II.) Special reactions.

I.—Group Reactions.

1. Heat the acid in a test tube—

Blackens instantly.	Fuses and blackens after a short time.	Forms a white sublimate, the residue blackening.	Not blackened. White sublimate.	Not blackened. Volatile.
Tartaric (caramel odor). Uric (burnt feather odor). Hippuric (benzene odor). Gallic. Tannic.	Citric.	Malic. Meconic. Pyrogallic.	Oxalic.	Acetic (yields acetone). Formic. Benzoic. Succinic. Butyric. Hydrocyanic. Phenic.

2. Heat the acid in a test tube with sulphuric acid—

Blackens instantly.	Blackens after a time.	Not blackened.	Volatile.
Tartaric. Pyrogallic. Gallic (red). Tannic (brown). Hippuric.	Citric. Malic. Uric. Meconic.	Oxalic. Evolves CO_2 and CO. Sulphocyanic. Evolves CSO, giving odor of SO_2. Hydrocyanic and other cyanogen acids. Evolve CO and NH_3.	Acetic Formic Benzoic Succinic } Evolve CO.

3. Render the acid solution neutral, and add calcic chloride. Filter off the precipitate—

Precipitate. { If soluble in acetic acid=Tartaric acid.
If insoluble in acetic, but soluble in HCl=Oxalic acid.

Filtrate. { Boil with lime water; a precipitate indicates citric acid.
Boil for a long time with lime water and alcohol; a precipitate indicates malic acid.

4. Add to the acid solution ferric chloride—

A Red Coloration, but no ppt.	Other Reactions.
Acetic; color disappears with HCl. Formic; ,, ,, Pyrogallic; ,, ,, Sulphocyanic; color disappears with $HgCl_2$, but not with HCl. Meconic; color neither discharged by $HgCl_2$ nor by HCl.	Carbolic; purple. Gallic and tannic; black. Ferrocyanic; blue. Ferricyanic; brown (blue with $FeSO_4$). Benzoic, Succinic, Hippuric } light red.

5. Add to the neutral solution argentic nitrate.

White precipitates occur with the following acids, all of which are soluble in ammonia; viz.: hydrocyanic (insol. in HNO_3; sol. in KCy); sulpho-, ferro-, and ferri-cyanic; meconic; oxalic; succinic; benzoic; tartaric (*see* Tests); citric; malic; acetic. The silver salt is reduced by formic and pyrogallic acids.

6. Add to two portions of the solution, potassic hydrate and hydrochloric acid respectively—

Potassic Hydrate.	Hydrochloric Acid (to neutral solution).
Tartaric; white ppt. on addition of acetic acid. Gallic; green ppt. Tannic; brown ppt. Pyrogallic; black ppt.	Uric; white ppt. (powder). Benzoic; ,, (flakes). Hippuric; ,, (feathery-crystals, soluble in boiling water).

II.—Special Reactions.

Acetic Acid ($C_2H_4O_2$) and the **Acetates.**

1. The acid is soluble in all proportions in water, alcohol, and ether. It dissolves camphor and several resins.

2. *Heat.* The acid and its salts are decomposed, yielding acetone (C_3H_6O).

3. When a mixture of sodic acetate and soda lime is heated, it yields methane or marsh gas ($3NaC_2H_3O_2 + NaHOCa''H_2O_2$ (soda lime) $= 2Na_2CO_3 + CaCO_3 + 3CH_4$).

4. The acetates, heated with alcohol and sulphuric acid, yield the fragrant ethylic acetate ($C_2H_5.C_2H_3O_2$) (*characteristic*).

5. The solid salts, heated with sulphuric acid, yield acetic acid.

6. *Ferric chloride* gives on boiling a deep red coloration, with the precipitation of a basic ferric acetate.

Oxalic Acid ($C_2H_2O_4$).

1. *Heat;* (α) fuses; (β) gives a white sublimate if carefully

heated; (γ) produces dense white fumes towards the end of the reaction, *but never blackens.* (The oxalates of the alkalies and alkaline earths, when heated, leave carbonates, which effervesce with acids; but the oxalates of other metals leave metallic oxides.)

2. H_2SO_4 *and heat;* CO and CO_2 are evolved, but without blackening. (The reaction with the oxalates is similar, a residue of sulphate remaining.)

3. *Calcic chloride* ($Ca''Cl_2$) gives (α) *in very dilute solutions* a ppt., after a time, of calcic oxalate, $Ca''C_2O_4$; (β) in *moderately strong solutions*, it gives an immediate ppt. The ppt. is soluble in HCl and in HNO_3 (but not in acetic acid, as in the case of phosphates) and is reprecipitated by ammonia.

The reaction is not interfered with by the presence of ammoniacal salts.

4. *Argentic nitrate* gives a white ppt., $Ag_2C_2O_4$.

Uric Acid ($C_5N_4H_4O_3$).

1. *Heat;* (α) blackens immediately; (β) odor of burnt hair.

2. A drop of *nitric acid*, mixed with uric acid in a capsule, and evaporated to dryness, yields, when the cold residue is touched with ammonia, the deep red tint of murexide ($C_8N_6H_8O_6$).

Hippuric Acid ($C_6H_9NO_3$).—*Crystals;* rhombic prisms, and acicular crystals.

1. *Heat;* (α) fuses directly, and volatilizes with partial decomposition, yielding benzoic acid, ammonic benzoate, and benzo-nitrile; (β) a carbonaceous residue left; any sublimate formed is of a red tint; (γ) odor of benzo-nitrile.

[N.B. Hippuric acid is insoluble in ether, but benzoic acid is soluble.]

The hippurates, when fused with excess of potassic hydrate, give off ammonia, and yield benzene by distillation.

Citric Acid ($C_6H_8O_7$).—1. *Heat;* (α) does not blacken immediately; (β) evolves pungent acid fumes; (γ) blackens ultimately (distinguishes it from malic acid).

2. *Sulphuric acid and heat* blackens the acid, but not immediately (distinguishes it from tartaric acid).

3. *Calcic chloride* gives no ppt. on boiling in a solution of the free acid, but on neutralizing the solution with KHO a white insoluble ppt. of calcic citrate is thrown down. The ppt. is insoluble in KHO (distinguishing it from calcic tartrate), but is soluble in NH_4Cl. Boil the ammonic chloride solution, when a white ppt. is thrown down, which is no longer soluble in NH_4Cl.

4. *Calcic citrate* heated with ammonia and argentic nitrate, yields no metallic mirror, thus distinguishing it from tartaric acid.

Malic Acid ($C_4H_6O_5$).—*Crystals;* colorless prisms.

1. *Heat* chars the acid, and yields fumaric acid.

2. *Calcic chloride;* no ppt. in very dilute aqueous solutions, but a ppt. forms when alcohol is added (calcic malate).

3. *Plumbic acetate,* in neutral solutions a white ppt. (plumbic malate), *sparingly soluble in ammonia*, distinguishing it from plumbic citrate and tartrate, which dissolve easily.

Tartaric Acid ($C_4H_6O_6$).

1. *Heat;* (α) blackens immediately; (β) caramel odor; (γ) gives no sublimate.

2. H_2SO_4 *and heat;* (α) blackens immediately; (β) caramel odor. (Reaction similar with tartrates.)

3. *Potassic* (*chloride* or) *acetate* gives a precipitate (with moderately strong solutions) of acid potassic tartrate, $KHC_4H_4O_6$. The delicacy of this reaction is increased—(α) by shaking; (β) by the addition of alcohol.

4. *Calcic chloride* (*in excess*) gives, in moderately strong solutions, an immediate white precipitate of calcic tartrate, $Ca''C_4H_4O_6$, which rapidly becomes crystalline. The precipitate is soluble in KHO or NaHO. Ammoniacal salts prevent the reaction.

Filter off the precipitate and dry gently. Place it in a test-tube with a drop of ammonia and a crystal of argentic nitrate, and heat very gently, when a brilliant silver mirror will be obtained. (This distinguishes it from citric acid.)

5. *Lime and baryta waters, and plumbic acetate;* white precipitates, soluble in excess of acid.

6. *In neutral solutions of tartrates:—*

Argentic nitrate; a white precipitate, soluble in ammonia.

Calcic chloride; a white precipitate.

N.B.—Tartaric acid interferes with the precipitation of ferric hydrate by ammonia, owing to the solubility of the hydrate in a tartaric acid solution.

Benzoic Acid ($C_7H_6O_2$), *Crystals*, prismatic needles.

1. *Heat;* (α) *in a test tube;* melts at 212° F. (100° C.), and a little above this sublimes; emits an aromatic odor; (β) *on platinum foil;* burns with a smoky flame.

2. *Sulphuric acid* and *heat* does not blacken, but dissolves the acid.

3. *Nitric acid;* no action.

4. Distilled with excess of CaO, yields benzene—($C_7H_6O_2 + CaO = C_6H_6 + CaCO_3$).

5. *Ferric chloride;* a pale, yellow-brown precipitate of basic ferric benzoate.

Succinic Acid ($C_4H_6O_4$); *Crystals;* oblique, rhombic prisms.

1. *Heat;* (α) *in test tube;* melts at 356° F. (180° C.), and sublimes in silky needles, emitting an irritating odor; (β) *on platinum foil;* burns with a blue flame, without smoke.

2. *Ferric chloride* gives, in neutral solutions, a brownish-red preci-

pitate of basic ferric succinate, soluble in mineralacids; darkened by ammonia.

3. *Nitric acid,* no action.

Note the distinctions between benzoic and succinic acids, as follows :—

1. Benzoic acid heated on platinum foil burns with a smoky flame, while succinic acid does not.

2. *Ferric chloride* gives a brown precipitate with both acids. Treat this with ammonia. One portion is decomposed, whilst another forms a soluble succinate and benzoate. Filter, and add alcohol and baric chloride to the clear filtrate :—

(*α*.) With a *ferric succinnate,* a white crystalline precipitate is formed.

(*β*.) With a *ferric benzoate,* no precipitate is formed.

Tannic Acid—

1. *Heated in tube,* fuses, blackens immediately, and gives no sublimate.

2. *Sulphuric acid and heat;* turns dark brown. (*See* Gallic Acid, which turns red.)

3. *Nitric acid and heat,* a yellow solution, turning red on boiling.

4. *Ferric chloride,* a black precipitate and coloration.

Gallic Acid—

1. *Heated in tube,* fuses, blackens immediately, giving an orange-red sublimate.

2. *Sulphuric acid and heat;* turns magenta red, becoming more intense as the heat increases. (*See* Tannic Acid, which turns brown.)

3. *Nitric acid and heat;* same as Tannic Acid.

4. *Ferric chloride;* same as Tannic Acid.

Hydrocyanic Acid (*see* page 619).

Ferrocyanic Acid (*see* page 620) ($H_4Fe''Cy_6$).

1. Reaction acid; decomposes alkaline carbonates; stable.

2. *Ferrous sulphate;* a light blue ppt., $K_2Fe.FeCy_6$.

3. *Ferric chloride;* a deep blue ppt. (prussian blue) $Fe'''_4Fe''_3Cy_{18}$.

Ferricyanic Acid (*see* page 620) ($H_3Fe'''Cy_6$).

1. An unstable acid.

2. *Ferrous sulphate;* a deep blue ppt. (Turnbull's blue) $Fe''_3Fe'''_2Cy_{12}$.

3. *Ferric chloride;* a deep brown coloration.

Sulphocyanic Acid (*see* page 620) (HCNS).

1. Reaction acid; easily decomposed.

2. *Ferric chloride;* a blood-red coloration, but no ppt., even on boiling; *color discharged by mercuric chloride* ($HgCl_2$).

Meconic Acid ($C_7H_4O_7$).

1. *Ferric chloride;* a blood-red coloration; *color not discharged by mercuric chloride.*

SUPPLEMENTARY CHAPTER.

Supplement to the Fatty Acids (page 706).

Fats and Oils.

Definition.—The fats and oils are combustible bodies, having an unctuous feel, communicating a greasy stain to paper, insoluble in water, but soluble in alcohol and in ether. They are all compounds of glycerine with palmitic, oleic, or stearic acid.

Natural History.—They are found in all parts of the vegetable, but chiefly in the seeds (rape) and fruit (olive). They also occur in the animal, formed by the conversion of starch and saccharine matters, and are found located chiefly under the cuticle, or in the omentum or round the kidneys. The fat is generally lodged in cells, the envelope of which consists of cellulin or gelatinous tissue. Fat not unfrequently occurs as a product of tissue degeneration (as in the kidney, liver, etc.), and is also found as a product of secretion (as in milk).

Preparation.—(1.) *By simple pressure* (croton, olive, almond, linseed, mustard, etc.).

(2.) *By heat and pressure,* as in the case of the solid fats (such as lard, human, cod-liver (dark colored), castor (hot drawn), etc.)

(3.) *By cold and pressure* (castor and cod-liver (cold drawn), lard).

(4.) *By distillation* (volatile oils).

(5.) *By destructive distillation* (coal-tar oils).

(6.) *By solution in a fixed oil, in alcohol or in ether* (yelk oil).

(7.) *By fermentation* (oil of bitter almonds).

Classification.

I. *Fixed oils;* that is, oils which decompose at a temperature below that at which they distil, and impart a *permanently* greasy stain to paper.

II. *Volatile oils;* that is, oils which may be distilled unchanged, and that impart a greasy stain to paper, which is not permanent.

I. Fixed Oils.

The fixed oils are composed of two or more neutral substances, combined with some of the acids of the acetic series, or with acids closely allied to them.

These are divided into two classes :—

(A.) *Saponifiable oils.*

(B.) *Non-saponifiable oils.*

(A.) **Saponifiable Fixed Oils.**—Some of these are *solid*, as, *e.g.*, palm oil; and some are *liquid*, as, *e.g.*, olive oil. Of animal fats, those from *warm*-blooded animals are usually solid at ordinary temperatures (such as suet); whilst those from *cold*-blooded animals are commonly liquid (such as the fish oils). The fats and oils have very little odor or taste. Their specific gravities vary from 0·91 to 0·94.

The action of heat.—The liquid oils may be solidified by cold. The solid fats melt at from 70° to 140° F. (21·1° to 60° C.) At 500° F. (260° C.) they usually undergo slight decomposition. At about 600° F. (315·5° C.) (that is, below the temperature at which they distil—hence they are termed *fixed oils*), they decompose, giving off carbonic anhydride and acrolein. At a higher temperature, as, *e.g.*, when dropped on a red-hot iron plate, they are decomposed into various hydrocarbons (oil gas).

Solubility.—They are all insoluble in water, but soluble in boiling alcohol and in cold ether. They are solvents of sulphur, phosphorus, etc.

Action of Air.—(*a.*) *Rancidity.* By exposure to air the oils commonly turn rancid. This, however, does not occur in the case of pure oil. Rancidity is brought about by the presence in the oil of certain albuminous matters, which, during decay, decompose the glyceric oleate, or the glyceric salts of other acids.

(*β.*) *Drying and non-drying oils.*—Most fats and oils, when exposed to the air, absorb oxygen (some at the same time evolving carbonic anhydride), ultimately becoming solid. These are called "drying oils," of which linseed, rape, and mustard are illustrations. They contain glyceric oleate (olein), or glyceric salts of acids homologous to oleic acid. This oxidation process has, in some cases, been so rapid that active combustion has resulted. This property of drying is, in many cases, increased by dissolving in the oil when hot a twentieth part of its weight of litharge or oxide or borate of manganese. This constitutes (as in the case of linseed) what is called "boiled oil." Other oils do not absorb oxygen;—chemically, they differ from the drying oils in containing glyceric salts of acids other than those belonging to the oleic series, such as glycerides of linoleic acid, ($C_{16}H_{28}O_2$); nevertheless, they gradually alter by exposure, though in a different manner. These are called "non-drying oils," such as olive, almond, rape-seed, etc.

The oils are all decomposed by the action of the haloids.

Acids act on them, forming various compounds.

With the fixed alkalies they form salts called soaps (saponification).

Potash forms with them a soft soap, and soda a hard soap. Ammonia does not form a true soap with the oils, but compounds called amides.

The fats combine with metallic oxides and hydrates to form plasters, glycerin being set free. Thus :—

$$\begin{array}{ccccccccc} 3PbO & + & 3H_2O & + & 2(C_3H_5\cdot 3C_{18}H_{33}O_2) & = & 3(Pb2C_{18}H_{33}O_2) & + & 2(C_3H_5 3HO). \\ \text{Plumbic oxide} & + & \text{Water} & + & \text{Oleate of glyceryl (olive oil)} & = & \text{Oleate of lead (lead plaster)} & + & \text{Glycerin.} \end{array}$$

The following is a tabulated list of the principal fats and oils :—

Name.	Source.	Sp. Gr.	Fusibility. F.	
1. *Non-drying Oils.*				
Olive	Olea europæa	0·918	Solid below 32° F. (0° C.)	*Virgin oil* is the oil obtained by pressure without heat.
Almond	Amygdalus communis	0·918 at 60° F.	Solid below —13° F. (—25° C.)	Seeds yield 50 per cent. of oil.
Sesamé	Sesamum indicum			
Rapeseed				
Mustard	..	..	..	Yields crucic acid on saponification.
Colza	Brassica oleifera	0·913		
Yelk				
Male fern ..	Filix mas	..	..	Contains filicic acid, $C_{14}H_{14}O_5$
Human	..	..	..	Contains olein and margarine.
2. *Drying Oils.*				
Linseed	Linum usitatissimum	1·939 at 54° F.	Solid at —15° C.	25 per cent. extracted from seed; 12 per cent. left in the cake.
Walnut	..	..	Liquid at ordinary temperatures.	
Hempseed ..	..	..		
Poppyseed ..	..	..		
Croton	..	..	..	Tiglic acid, but not crotonic acid, is obtained from the oil.
Castor	Ricinus communis	0·969	Solid at —14° F. (—25·6° C.)	A *ricinoleate* of glyceryl $(C_3H_53C_{18}H_{33}O_3)$.
3. *Fish Oils.*				
Sperm	*Liquid* fat in head of spermaceti whale.	0·868	Solid at 45° F. (7·2° C.)	Contains phocenin.
Common whale	Common whale	0·927	Solid at 32° F. (0° C.)	
Cod liver	Gadus morrhua	..	Solid at 30° F. (—1° C.)	Contains constituents of bile; also a phosphorized fat (the oil gives a crimson with H_2SO_4).
4. *Solid Fats.*				
Tallow	Fat of ox, sheep, etc.	..	..	Suet; almost entirely stearine.
Lard	Soft fat of pig			
Butter	Milk			
Palm	Elais guineensis	..	81° F. (27·2° C.)	Becomes more solid by keeping.
Nutmeg butter	Myristica	..	87° F. (30·5° C.)	Volatile oil and myristin $(C_3H_53C_{14}H_{27}O_2)$.
Cocoa nut ..	Cocos nucifera	..	68° F. (20° C.)	Contains glycerin, combined with caproic, caprylic, lauric, myristic, and palmitic acids. Used for marine soap, being soluble in NaCl.
Cacao butter ..	Theobroma cacoa	..	85° F. (29·5° C.)	Chiefly stearine.
Laurel fat ..				
Yellow wax ..	Honeycomb of bee	0·96	145° F. (63° C)	White wax is the yellow wax bleached. Contains cerolein (5 per cent.) and cerotic acid.
Spermaceti ..	*Solid* fat in head of spermaceti whale	0·940	120° F. (49° C.)	Palmitate of cetyl yields ethal (not glycerine) on saponification.

The following Table, from Bloxam, shows the principal fatty bodies, and their corresponding acids and fusing points.

Neutral Fats.	Formulæ.	Chief Source.	Fusing Point. ° F.	Fatty Acids.	Formulæ.	Fusing Point. ° F.
Stearin ..	$C_{57}H_{110}O_6$	Tallow	125 to 157	Stearic.	$C_{18}H_{36}O_2$	159
Palmitin ..	$C_{51}H_{98}O_6$	Palm oil.	114 to 145	Palmitic.	$C_{16}H_{32}O_2$	144
Margarin ..	$C_{54}H_{104}O_6$	Olive oil.	116	Margaric.	$C_{17}H_{34}O_2$	140
Olein	$C_{57}H_{104}O_6$	Do.	Below 32	Oleic.	$C_{18}H_{34}O_2$	40
Cetin	$C_{32}H_{64}O_2$	Spermaceti.	120	Palmitic.	$C_{16}H_{32}O_2$	144
Myricin ..	$C_{46}H_{92}O_2$	Bees'-wax.	162	Do.		

(B.) **Nonsaponifiable Fats.**—This includes certain bodies, such as cetene and ethal from spermaceti, myricin and ceren from bees'-wax, cholesterin, etc.

They are all solid crystalline bodies, and fuse at temperatures varying from 180° to 300° F. (82° to 149° C.)

II.—Volatile Oils. (*See* page 650.)

Soaps.

A soap results from the action of alkalies on fats and oils. If potash be used for effecting saponification, a soft soap results ; if soda, a hard soap. Tallow, palm-oil, cocoa-nut oil, and kitchen stuff are the fats commonly employed in the manufacture of hard soap, whilst seal and whale oil are used for soft soap. We may here note that—

(*a.*) *Tallow* consists of about three parts of solid stearin (or the glyceride of stearic acid), and one part of liquid olein (or the glyceride of oleic acid).

(*β.*) *Palm oil* consists chiefly of solid palmitin (or the glyceride of palmitic acid) and olein.

(*γ.*) *Seal and whale* oils consist chiefly of olein.

I. *Hard soaps.*—The fat is first boiled in a soda ley. When perfectly dissolved a quantity of common salt is added (*salting out*). The soap immediately rises to the surface, being insoluble in a solution of common salt. Thus an insoluble sodic stearate (or, if palm-oil be used, sodic palmitate) and sodic oleate are formed, whilst the glycerin remains in solution. Thus :—

$$(a.)\quad \underset{\text{Stearin; or glyceride of stearic acid}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\text{Caustic soda}}{3NaHO} = \underset{\text{Sodic stearate}}{3NaC_{18}H_{35}O_2} + \underset{\text{Glycerin.}}{C_3H_5(OH)_3.}$$

$$(\beta.)\quad \underset{\text{Olein; or glyceride of oleic acid}}{C_3H_5(C_{18}H_{33}O_2)_3} + \underset{\text{Caustic soda}}{3NaHO} = \underset{\text{Sodic oleate}}{3NaC_{18}H_{33}O_2} + \underset{\text{Glycerin.}}{C_3H_5(OH)_3.}$$

The soap, that is, the sodic stearate and oleate, is then allowed to collect on the surface, whilst the alkaline ley containing the glycerine is drawn off from below. The soap is then pressed in iron moulds. If *tallow* has been used, the soap is a mixture of *stearate* and oleate of soda; but, if *palm oil*, of *palmitate* and oleate of soda.

Transparent soaps are prepared by first drying the soap, then dissolving it in spirits of wine by heat, and pouring the solution into moulds after a sufficient quantity of spirit has been removed by distillation, so that the solution may set perfectly when cold.

Glycerine soap consists of a mixture of the soap and the alkaline solution containing the glycerin, as small a quantity of water being used in the operation as possible.

In *silicated soap*, silicate of soda is mixed with the soap.

In the *common yellow soaps*, a quantity of common rosin is added.

Castile soap is made from olive oil, which contains the glycerides both of palmitic and stearic acids (margarine), as well as oleic acid. Hence Castile soap is mixed stearate, palmitate and oleate of soda.

The appearance of *mottled soap* depends on the presence of veins of oxide of iron. It is supposed to indicate that the soap is tolerably free from water.

II. *Soft soaps.*—In fish oil, which is the fat used for soft soaps, olein, or the glyceride of oleic acid, predominates. This, with a *potash ley*, yields *oleate of potash*, of which soft soaps are principally composed. The solution of the soft soap is not salted, but is simply evaporated to the necessary consistency. If common salt were used, the soft soap would be converted into a hard soda soap.

Candles.

Stearic acid is commonly employed in preference to tallow for candles, because it fuses at a much higher temperature 159° F. (70·5° C.).

I. *The old process of Saponification by Lime.*—The melted tallow is first mixed with lime and water, and the mixture subjected to the action of superheated steam. In this way an insoluble stearate and oleate of lime are formed. These are separated from the solution which contains the glycerin, and are decomposed by the action of sulphuric acid. The mixed stearic and oleic acids set free are submitted to pressure in a hydraulic press, whereby the oleic acid is squeezed out, and stearic acid, mixed with more or less palmitic acid, obtained.

II. *Saponification* (so-called) *by Sulphuric Acid.*—The fats (palm oil, cocoa-nut oil, or any kind of refuse fat), are first mixed in copper boilers with about one-sixth their weight of sulphuric acid, and the mixture heated by steam for some time to 350° F. (176·1° C.). The sulphuric acid converts a part of the glycerin into sulpho-glyceric acid ($C_3H_8O_3.SO_3$), and decomposes the remainder, a mixture of crude palmitic, stearic and oleic acids remaining (probably as sulpho-acids), together with a solid, fatty acid, called *eladic acid*, isomeric with, and derived from the liquid oleic acid. Thus it will be noted that the quantity of solid fats obtained by this process is increased. These fatty acids, after being collected and well washed, are distilled in a current of steam heated to 600° F. (315·5° C.), the oleic acid being removed from the distillate by pressure. A pitchy matter remains in the retort, which is used in the manufacture of black sealing-wax.

III. *Saponification* (so-called) *by Steam.*—The advantage of this process is that the glycerin can be obtained at once in a pure state. It consists in merely distilling the fat by the action of superheated steam at 600° F. (315·5° C.), when both glycerin and fatty acids distil over. After the distillate has stood for a short time, the fatty acids collect on the surface of the glycerin, and on removal may be at once subjected to pressure to separate the oleic acid. The glycerin, as obtained by this process, is at once fit for the market.

The Tannins.

The Tannins are a class of amorphous bodies, widely distributed, constituting the astringent principles of plants. Our knowledge of these bodies, which are probably modifications of tannic acid, is very limited. The following special reactions are to be noted : —

1. They have all a slightly acid reaction, and a very astringent taste.
2. They yield a blue-black, and in some cases a green precipitate with ferric salts.
3. They precipitate albumen and gelatine from their solutions.
4. They form leather (a substance having a power of resisting putrefaction) with animal membranes. [NOTE.—Gallic acid does not possess this power.]

The tannic acid of the oak (*gallotannic acid*; $C_{27}H_{22}O_{17}$), or what is more probably a glucoside of tannic acid, is extracted by a mixture of water and ether from certain growths (called "nut-galls"), occurring on the leaves of the *Quercus infectoria*, and said to be produced by the puncture of an insect.

Tannic acid is a yellowish amorphous mass, resolved by heat into carbonic anhydride, pyrogallic and metagallic acids. It is soluble in water, the solution reddening litmus. When boiled with acids or with a strong solution of potash, it splits up into glucose and gallic acid, the same change occurring spontaneously when the powdered galls, mixed with water, are allowed to ferment. This fermentative process results from the presence in the nut-galls of a nitrogenized body, capable of acting as a ferment. The glucose formed ultimately undergoes alcoholic fermentation.

The tannins that turn ferric salts *black*, yield *pyrogallol* ($C_6H_6O_3$) on dry distillation; whilst those that turn ferric salts *green*, yield *pyrocatechin* ($C_6H_6O_2$).

Ink.—This consists of a mixture of nut-galls with water, gum, and ferrous sulphate. By standing, the ferrous salt is converted into a ferric salt, and a black tannate of ferric oxide (?) formed. A trace of creosote is usually added, to prevent the ink becoming mouldy. The brown color of old ink is due to the oxidation of the tannic acid leaving simply the brown ferric oxide. Ink leaves an iron-mould stain wherever it has fallen on linen after the fabric has been washed, from the removal of the tannic acid by the alkali of the soap.

Tanning.—The skin (that is to say, the dermis or true skin) is converted into leather by the action of tannic acid on the gelatine. The leather formed is tough, resists putrefaction, and is impermeable to water.

(*α*.) The skin is first soaked in lime-water for the purpose of saponifying the fat, and dissolving the sheath of the hairs, so that their removal may be easily effected.

(*β*.) After the skin has been cleansed and the hair removed, it is placed in very dilute sulphuric acid, in order that any adherent lime may be neutralized (otherwise a tannate of lime would be afterwards formed), and also to "raise the skin," that is, to open the pores to receive the tanning liquid.

(*γ*.) The skin is then placed in an infusion of oak-bark (*ooze*) for a few weeks, and, finally, a number of skins are arranged in layers in a pit, coarse ground oak-bark being placed between each skin. Sometimes sumach (the ground shoots of the *rhus coriaria*) is used in the place of oak-bark. On removal from the pit, the skins are dried in a free current of air.

Currying consists in wetting the leather first with water, and afterwards with oil. As the water evaporates, the oil sinks into the skin.

In *tawing* (as in the preparation of kid for gloves), the lime on the skin is removed by lactic acid, a sour mixture of bran and water being commonly employed. The skin is afterwards impregnated with aluminic chloride (a bath of alum and salt being commonly used), which effectually prevents putrefaction.

In *shamoying* (as in the preparation of wash-leather), the skin is first sprinkled with oil, and then beaten with wooden hammers. It is afterwards exposed to a warm atmosphere in order to dry the oil, any excess of oil being removed by a weak alkaline bath.

CHAPTER XXV.

THE ETHERS.

Oxy-Ethers—Ethers of Monohydric Alcohols—Preparation—Ethers of Di- and Trihydric Alcohols. Sulpho-Ethers. Haloid Ethers. Compound Ethers.

I. Oxy-Ethers.

These ethers are the oxides of alcohol radicals. The relationship subsisting between a *metallic hydrate*, as NaOH, and a *metallic oxide*, as Na_2O, has its counterpart in the relationship between *an alcohol* (that is, a hydrate of an alcohol radical) as *ethylic alcohol*, C_2H_5 (OH), and an *oxy-ether* (that is, an oxide of an alcohol radical) as *ethylic ether*, $(C_2H_5)_2O$.

Just, too, as we have monohydric, dihydric, and trihydric alcohols, so we have ethers of monohydric, dihydric, and trihydric alcohols respectively.

Ethers of Monohydric Alcohols.

Ethers.	Formulæ.	Boiling Pt.		Sp. Gr.	Remarks.
		° F.	° C.		
Methylic	$(CH_3)'_2O$	—5·8	—21	1·617	A colorless liquid. Does not liquefy at —16° C. Burns with a feebly luminous flame. The vapor is soluble in water (33 in 1), alcohol, wood spirit, and sulphuric acid. It forms substitution compounds with Cl, as $(CH_2Cl)_2O$, etc.
Methylic ethylic ..	$(CH_3)'(C_2H_5)'O$	51·8	11		
Methylic amylic ..	$(CH_3)(C_5H_{11})O$	197·6	92		
Ethylic (ether) ..	$(C_2H_5)'_2O$	96·0	35·6	0·723	
Ethylic butylic ..	$(C_2H_5)(C_4H_9)O$	176·0	80		
Ethylic amylic ..	$(C_2H_5)(C_5H_{11})O$	233·6	112		
Butylic	$(C_4H_9)''_2O$	219·2	104		
Amylic	$(C_5H_{11})'_2O$	348·8	176		
Allylic	$(C_3H_5)'_2O$	179·6	82		
Phenylic	$(C_6H_5)_2O$				
Benzylic	$(C_7H_7)_2O$				
Phenylbenzylic ..	$(C_6H_5)(C_7H_7)O$				

Preparation of the Simple and Mixed Ethers (General).

(I.) *The ethers derived from the alcohols of the methylic series* ($C_nH_{2n+1}OH$), *or of the vinylic series* ($C_nH_{2n-1}OH$).

Preparation.—By the action of sulphuric acid on the alcohol. The process takes place in two stages :—

(α.) The sulphuric acid first converts a portion of alcohol into a ulpho-acid :—

$C_2H_5(OH)$	+	H_2SO_4	=	$C_2H_5HSO_4$	+	H_2O.
Ethylic alcohol	+	Sulphuric acid	=	Sulpho-ethylic acid (sulphovinic acid)	+	Water.

(β.) This sulpho-acid then reacts on a fresh portion of alcohol :—

$C_2H_5HSO_4$	+	$C_2H_5(OH)$	=	$(C_2H_5)_2O$	+	H_2SO_4.
Sulpho-ethylic acid	+	Ethylic alcohol	=	Ethylic ether	+	Sulphuric acid.

[NOTE.—A. That the sulphuric acid concerned in the first stage of he reaction is set free in the second stage. Thus, theoretically, a mall quantity of acid should convert an unlimited quantity of alcohol nto ether.

B. That by boiling the ethers with dilute sulphuric acid they are onverted into their corresponding alcohols. Thus :—

(α.) $(C_2H_5)_2O + 2H_2SO_4 = 2[(C_2H_5)HSO_4] + H_2O$.

(β.) $(C_2H_5)HSO_4 + H_2O = H_2SO_4 + C_2H_5(OH)$.]

(II.) *The ethers derived from the alcohols of the ethylic series* $C_nH_{2n+1}OH$), *of the vinylic series* ($C_nH_{2n-1}OH$), *and of the benzylic series* $C_nH_{2n-7}OH$).

Preparation.—By the action of an iodide derivative of the coresponding hydrocarbon on the sodium or potassium derivative of the orresponding alcohol.

Thus, to prepare ethylic ether two stages may be noted :

(α.) By the action of sodium on ethylic alcohol, we first form a odium derivative :—

$2C_2H_5.OH$	+	Na_2	=	$2C_2H_5.NaO$	+	H_2.
Ethylic alcohol	+	Sodium	=	Sodic ethylic alcohol	+	Hydrogen.

(β.) By the action of ethylic iodide (C_2H_5I) on the sodic ethylic lcohol, we form ethylic ether and sodic iodide :—

$C_2H_5(NaO)$	+	C_2H_5I	=	$(C_2H_5)_2O$	+	NaI.
Sodic ethylic alcohol	+	Ethylic iodide	=	Ethylic ether	+	Sodic iodide.

It will be seen that *a simple ether* is formed when the haloid erivative acts on a metallic derivative of *a corresponding* alcohol, *.g.*, when *ethylic* iodide acts on sodic *ethylic* alcohol, ethylic ether, $C_2H_5)O$, is formed : but that a *mixed ether* will be produced when he haloid derivative acts on the metallic derivative of some *isomeric* r *homologous* alcohol ; *e.g.*, when *ethylic* iodide acts on sodic *methylic* lcohol, methylic ethylic ether $(CH_3)(C_2H_5)O$ is formed.

(III.) Phenylic ether is prepared by fusing together phenol and diazo-benzene sulphate. Thus :—

$$\underset{\text{Diazobenzene sulphate}}{C_6H_5(N_2HSO_4)} + \underset{\text{Phenol}}{C_6H_5(OH)} = \underset{\text{Phenylic ether}}{(C_6H_5)_2O} + \underset{\text{Nitrogen}}{N_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4.}$$

Ethylic Ether.—*Ethyl Oxide; Common Ether* $(C_2H_5)_2O$.

Preparation.—(1.) By the action of ethylic iodide on sodium ethylate.

$$NaC_2H_5O + C_2H_5I = (C_2H_5)_2O + NaI.$$

(2.) By dehydrating alcohol by means of sulphuric acid. This reaction takes place in two separate stages :—

$$(\alpha.)\ C_2H_5,HO + H_2SO_4 = C_2H_5.HSO_4 + H_2O.$$
$$(\beta.)\ C_2H_5.HSO_4 + C_2H_5.HO = (C_2H_5)_2O + H_2SO_4.$$

Properties.—Ether is a colorless mobile liquid, with a peculiar odor and burning taste. It is combustible, and when the vapor is mixed with air or oxygen it explodes. (Sp. gr. of vapor = 2·586.) Slightly soluble in water, and miscible in all proportions with alcohol. Ether does not freeze, but when moist ether is cooled it forms a cryohydrate ($C_4H_{10}O.2H_2O$).

When heated with dilute sulphuric acid it is converted into alcohol. On exposure to air it is slowly converted into acetic acid. With hot nitric acid it forms carbonic, acetic, and oxalic acids, and with chlorine it forms substitution products.

Uses.—It is used in the arts and manufactures, as well as in the laboratory, as a solvent for oils and fats; also for the preparation of collodion ; in medicine, in the form of a spray, to produce cold and effect local anæsthesia ; also as a general anæsthetic agent.

Ethers of Dihydric Alcohols.

ETHER.	Formulæ.	Boiling Point.	
		° F.	° C.
Ethylenic	C_2H_4O	55·4	13·0
Propylenic	C_3H_6O	63·0	35·0
Amylenic	$C_5H_{10}O$	171·0	95·0

Preparation (general).—By the action on the glycols (dihydric alcohols) (*a*), first, of hydrochloric acid, whereby *a chlorhydrin* is formed; and (*β*), afterwards, by the withdrawal of hydrochloric acid from the chlorhydrin, by the action of potassic hydrate. These two stages are seen in the preparation of ethylenic ether, as follows :—

$$(\alpha.)\ C_2H_4(OH)_2 + HCl = C_2H_4(OH)Cl + H_2O.$$

Glycol + Hydrochloric acid = Ethylenic chlorhydrate + Water.

$$(\beta.)\ C_2H_4(OH)Cl + KHO = C_2H_4O + KCl + H_2O.$$

Ethylenic chlorhydrate + Potassic hydrate = Ethylenic ether + Potassic chloride + Water.

Ethylenic Ether; *Ethylenic oxide* (C_2H_4O). *Molecular weight*, 44. *Molecular volume*, ☐☐. *Boils at* 56·3° F. (13·5° C.).

Preparation.—(Described above.)

This ether is the only one of the ethers of the dihydric alcohols that has received much attention.

It combines *with acids* as a base; thus, $C_2H_4O + HCl = C_2H_4(OH)Cl$.

It combines *with water* to form glycol; thus, $C_2H_4O + H_2O = C_2H_4(OH)_2$.

It precipitates many *metallic salts*, as hydrates, from their solutions; thus, $2C_2H_4O + MgCl_2 + 2H_2O = 2[C_2H_4(OH)Cl] + MgH_2O_2$.

With *nascent hydrogen* it forms alcohol; thus, $C_2H_4O + H_2 = C_2H_5(OH)$.

With *oxygen* it forms glycollic acid; thus, $C_2H_4O + O_2 = C_2H_4O_3$.

Ether of the Trihydric Alcohols.

Glycylic Ether, $(C_3H_5)_2O_3$, is the only ether of this class known. It is prepared by heating together glycerin and calcic chloride, the calcic chloride abstracting three molecules of water from the glycerin. Thus—

$$2(C_3H_5(OH)_3) = 3H_2O + (C_3H_5)_2O_3.$$

Glycerin = Water + Glycylic ether.

II.—Sulpho- or Thio-Ethers.

The sulpho-ethers bear the same relationship to the mercaptans that the ethers bear to the alcohols. Thus—

$$C_2H_5(OH)\ —\ C_2H_5.O.C_2H_5;\quad C_2H_5(SH)\ —\ C_2H_5.S.C_2H_5.$$

Alcohol — Ether ; Mercaptan — Sulpho-ether.

Preparation.—(1.) By the distillation of the lead derivatives of the mercaptans $[(C_2H_5S)_2Pb = (C_2H_5)_2S + PbS]$.

(2.) By the action either (α) of potassic or sodic sulphide, or (β) of the sodic or potassic derivatives of the mercaptans, on the monohaloid derivatives of certain hydrocarbons. Thus:—

$$(\alpha.)\ 2C_2H_5Br + K_2S = (C_2H_5)_2S + 2KBr.$$

$$(\beta.)\ C_2H_5I + C_2H_5(NaS) = NaI + (C_2H_5)_2S.$$

III.—Haloid Ethers.

These ethers are alcohols where a haloid element or a cyanogen group has been substituted for a semi-molecule of hydroxyl.

These compounds are formed either by the action on the alcohols (α) of the haloid acids, or (β) of the compounds of phosphorus with the haloids; or (γ) by the direct substitution of the haloids for hydrogen in saturated hydrocarbons. Thus :—

$$(\alpha.)\ C_2H_5(OH)+HCl=C_2H_5Cl+H_2O.$$
$$(\beta.)\ 3C_2H_5.OH+PCl_3=3C_2H_5Cl+H_3PO_3.$$
$$(\gamma.)\ CH_4+Cl_2=CH_3Cl+HCl.$$

The preparation of the nitriles is described elsewhere.

The composition and properties of the most important of the haloid ethers have been already described under the several hydrocarbons of which they are derivatives.

IV.—Compound Ethers.

These ethers are alcohols where the hydroxyl has been replaced by an acid radical. They are also called *ethereal salts.*

They are formed—

(1.) By the action of the acids on the alcohols ($C_2H_5OH+HNO_3=C_2H_5NO_3+H_2O$).

(2.) By heating a silver salt with an alcoholic iodide ($AgC_2H_3O_2+C_2H_5I = C_2H_3O_2.C_2H_5+AgI$).

The alcohol can be obtained from the compound ether by heating it with an alkali ($C_2H_5NO_3+KHO = C_2H_5OH+KNO_3$).

ETHEREAL SALT.	Formulæ.	Boiling Pt.		Sp. Gr.	Remarks.
		° F.	° C.		
Ethylic nitrite	$C_2H_5NO_2$		18	0·900	Solution in alcohol forms "sweet spirit of nitre."
Ethylic acetate.. ..	$C_2H_5C_2H_5O_2$		74	0·910	
Ethylic butyrate ..	$C_2H_5C_4H_7O_2$		121	0·910	"Essence of pine apple."
Propylic acetate ..	$C_3H_7.C_2H_3O_2$		102	0·913	
Amylic acetate	$C_5H_{11}C_2H_5O_2$		137	0·883	"Essence of Jargonelle pear."

CHAPTER XXVI.

THE ALDEHYDES.

(ALCOHOL DEHYDROGENATUM).

THE ALDEHYDES—Constitution—Preparation—Reactions—Aldehydes of the Acetic Series—Formic Aldehyde—Aldehydes of the Acrylic and Benzoic Series—Other Aldehydes.

The aldehydes are formed from the alcohols by the simple withdrawal of hydrogen. Thus an aldehyde occupies an intermediate position between an alcohol and an acid, containing, in the case of the aldehydes of monohydric alcohols, two hydrogen atoms less than the corresponding alcohol, and one oxygen atom less than the corresponding acid. Thus—

$$CH_3.CH_2OH \; ; \qquad CH_3.COH \; ; \qquad CH_3.COOH.$$

Ethylic alcohol; Acetic aldehyde; Acetic acid.

There are reasons to believe that the hydrogen of the alcohol displaced to form an aldehyde, is the H_2 of the group CH_2OH. Hence it is customary to represent an aldehyde of a monohydric alcohol by the formula $R'COH$, and an aldehyde of a dihydric alcohol by the formula $R''(COH)_2$, etc. The aldehydes of monohydric and of dihydric alcohols only are known.

The following are the formulas of the aldehydes of monohydric alcohols:—

Acetic series of aldehydes		$C_nH_{2n+1}COH.$
Acrylic	„	$C_nH_{2n-1}COH.$
		$C_nH_{2n-5}COH.$
Benzoic	„	$C_nH_{2n-7}COH.$
		$C_nH_{2n-9}COH.$

Preparation.—(General methods.)

(1.) *From the alcohols;* by oxidation, as *e.g.*, by atmospheric air; by the action of chlorine on the dilute alcohol; by the action of dilute sulphuric acid and potassic bichromate, etc. Thus—

$$C_2H_5(OH) \quad + \quad O \quad = \quad CH_3COH \quad + \quad H_2O.$$

Ethylic alcohol + Oxygen = Acetic aldehyde + Water.

(2.) *From the acids;* by the dry distillation of calcic, sodic or potassic formate with the corresponding metallic salt of a monobasic acid. Thus—

$$COH(OK) \quad + \quad CH_3CO(OK) \quad = \quad CH_3COH \quad + \quad K_2CO_3.$$

Potassic formate + Potassic acetate = Acetic aldehyde + Potassic carbonate.

Reactions :—

NOTE.—(1.) *Their conversion into the corresponding alcohols.*—By the action of nascent hydrogen (*e.g.*, by the action of water on sodium amalgam). Thus—

$$CH_3COH + H_2 = C_2H_5(OH).$$

Acetic aldehyde + Hydrogen = Ethylic alcohol.

(2.) *Their conversion into the corresponding acids.*—By oxidation (*e.g.*, by the action of air). Thus—

$$CH_3COH + O = CH_3COOH.$$

Acetic aldehyde + Oxygen = Acetic acid.

(3.) *Their conversion into the potassic salts of the corresponding acids.*—By fusion with potassic hydrate. Thus—

$$CH_3.COH + KHO = CH_3CO(OK) + H_2.$$

Acetic aldehyde + Potassic hydrate = Potassic acetate + Hydrogen.

(4.) *Their conversion into chloraldehydes* (*i.e.*, Cl_2 being substituted for O).—By the action of phosphoric chloride. Thus—

$$CH_3(COH) + PCl_5 = CH_3(CCl_2H) + PCl_3O.$$

Acetic aldehyde + Phosphoric chloride = Chlor-aldehyde + Phosphoric oxytrichloride.

(5.) *Their conversion into acid chlorides.*—By the action of chlorine or bromine. Thus—

$$CH_3(COH) + Cl_2 = HCl + CH_3(COCl).$$

Acetic aldehyde + Chlorine = Hydrochloric acid + Acetyl chloride.

The aldehydes form crystalline compounds with the acid sulphites of the alkali metals. The aldehydes of the acetic series form *with ammonia*, aldehyde ammonias. They also unite with aniline to form *phenylated aldines*, and with urea to form *ureides*. They also combine with hydrocyanic acid.

Aldehydes of the Acetic Series ($C_nH_{2n+1}COH$).

NAME.	Formulæ.	Fusing Point.		Boiling Point.	
		° F.	° C.	° F.	° C.
Formic aldehyde ..	H,COH				
Acetic ,, ..	CH_3,COH			69·8	21
Propionic ,, ..	C_2H_5,COH			118·4	48
Butyric ,, ..	$C_3H_7(\alpha)COH$			167·0	75
Isobutyric ,, ..	$C_3H_7(\beta)COH$			143·6	62
Valeric ,, ..	$C_4H_9(\alpha)COH$			217·4	103
Isovaleric ,, ..	$C_4H_9(\beta)COH$			199·4	93
Caproic ,, ..	$C_5H_{11}(\beta)COH$			249·8	121
Œnanthylic ,, ..	$C_6H_{13}(\alpha)COH$	10·4	—12	305·6	152
Cuprylic ,, ..	$C_8H_{16}O$			352·4	178
Palmitic ,, ..	$C_{16}H_{32}O$	125·6	52		

Formic Aldehyde (*Methylic Aldehyde*) $HCOH$. A gaseous body.

Preparation.—By the action of an incandescent platinum wire on a mixture of air and the vapor of methylic alcohol.

Acetic (or **Ethylic**) **Aldehyde** ($CH_3.COH$) (often simply called *aldehyde*). *Molecular weight,* 44. *Molecular volume,* ☐☐. *Sp. gr.,* 0·805. *Boils at* 69·8° F. (21° C.).

Preparation.—By distilling a mixture of spirits of wine, water, sulphuric acid and manganese dioxide. The distillate is re-distilled with calcic chloride, then mixed with ether and saturated with dry ammonia gas. Crystalline ammonium aldehyde separates. This ammonium aldehyde distilled with dilute sulphuric acid yields aldehyde.

Properties.—A colorless, volatile and very acrid liquid, soluble in water in all proportions, having a neutral reaction, but becoming acid (acetic acid) on exposure to air. So great is its attraction for oxygen that it reduces the salts of silver to the metallic state. Thus by heating a mixture of aldehyde and argentic nitrate with a trace of ammonia in a test tube, the silver is deposited as a brilliant metallic mirror on the sides of the tube. When treated with potassic hydrate, aldehyde is decomposed, and a brown substance formed, called "resin of aldehyde." With hydrochloric acid it forms *aldol* ($C_4H_8O_2$).

There are three isomeric modifications of aldehyde, *viz.*—

Metaldehyde; crystalline; sublimes at 248° F. (120° C.).

Paraldehyde; liquid; boils at 257° F. (125° C.).

Elaldehyde; crystalline; fuses at 35·6° F. (2° C.); boils at 201·2° F. (94° C.).

Chloral, $CCl_3(COH)$.—By the action of chlorine, aldehyde is transformed into the compound called chloral or trichloraldehyde, the H_3 of the CH_3 being replaced by Cl_3. Thus—

$$\underset{\text{Acetic aldehyde;}}{CH_3.COH\ ;} \qquad \underset{\text{Chloral.}}{CCl_3.COH.}$$

Properties.—Chloral is a colorless liquid (specific gravity 1·5) boiling at 201·2° F. (94° C.). It combines rapidly with water to form *chloral hydrate* ($CCl_3.COH,H_2O$). By oxidation it forms *trichloracetic acid,* $CCl_3CO(OH)$, and by the action of nascent hydrogen it is reduced to aldehyde. By the action of alkalies it is at once decomposed into chloroform and a formate ($CCl_3COH+KHO=CCl_3H+HCO(OK)$).

Chloral Hydrate, $CCl_3.COH+H_2O$.

Preparation.—By the direct union of chloral with water.

Properties.—White crystalline solid, easily soluble in water and in alcohol. Melts at 51° C. and has a specific gravity of 1·8.

Uses.—In medicine it is used to produce sleep.

Acetal.—When gaseous hydrochloric acid is passed into a solution of aldehyde in anhydrous alcohol, a compound of aldehyde and ethylic chloride is formed, which, by heating with sodic ethylate, forms a compound of aldehyde and ethylic oxide called *acetal* $(C_6H_{14}O_2)=C_2H_4(OC_2H_5)_2$. Acetal is a colorless liquid; specific gravity 0·821°, boiling at 284° F. (140° C.). Under the action of platinum black it forms, first, aldehyde, and afterwards acetic acid.

Aldehydes of the Acrylic Series $(C_nH_{2n-1}COH)$.

Of this series two members are known.

NAME.	Formulæ.	Boiling Point.		
		° F.	° C.	
Acrylic aldehyde (acrolein).	C_3H_4O	126·5	52·5	A colorless mobile liquid. By oxidation it forms acrylic acid $(C_3H_4O_2)$.
Crotonic aldehyde	C_4H_9O	220·1	104·5	

Aldehydes of the Benzoic Series $(C_nH_{2n-7}COH)$.

The following members are known:—

ALDEHYDE.	Formulæ.	Boiling Point.		
		° F.	° C.	
Benzoic .. .. (Bitter almond oil; Benzaldehyde).	$C_6H_5(COH)$	356·0	180·0	*Preparation.*—(1.) By the oxidation of amygdalin. (2.) By digesting bitter almonds with water (action of synaptase on amygdalin). *Properties.*—A colorless liquid, Sp. gr. 1·043. Absorbs oxygen from the air, becoming benzoic acid.
Paratoluic	$C_6H_4(CH_3)(COH)$	399·2	204·0	
Alpha-toluic ..	$C_6H_5CH_2(COH)$			
Cumic	$C_6H_4(C_3H_7)(COH)$	456·8	236·0	Present in the essential oil of cumin, and in that of the water hemlock.
Sycocerylic ..	$C_{18}H_{28}O$			

Salicylic aldehyde (salicylol), an oxy-benzoic aldehyde $C_6H_4(OH)COH$, is a fragrant oil, boiling at 385·7° F. (196·5° C.), found in the flowers of the meadow-sweet (*spiræa ulmaria*). By oxidation it forms salicylic acid.

Anisic aldehyde $(C_6H_4(OCH_3)COH)$ is a fragrant oily liquid, boiling at 476·6° F. (247° C.), formed by the oxidation of oil of aniseed.

Aldehydes of Series ($C_nH_{2n-9}COH$).

This includes *cinnamic aldehyde*, $CH(C_6H_5)CH.COH$, the essential constituent of oils of cinnamon and cassia. By oxidation it forms cinnamic acid.

Aldehydes of the Dihydric Alcohols.

Of these the only one of any importance is—

Glyoxal, or *oxalic aldehyde* $(COH)_2$, which may be prepared by oxidizing alcohol with nitric acid. It forms, by oxidation, *glyoxalic acid*, $COH\ (COOH)$.

CHAPTER XXVII.

THE KETONES.

Constitution—General Preparation—Properties and Reactions.

A KETONE is a derivative of an aldehyde, in which the hydrogen atom of the group COH is replaced by an alcohol radical. Thus :—

Acetic aldehyde, CH_3COH, forms $(CH_3)_2CO$, *acetone.*

Propionic aldehyde, C_2H_5COH, forms $(C_2H_5)_2CO$ *diethyl ketone.*

The ketones may also be regarded, either as compounds of carbonic oxide with monad alcoholic radicals, as $(CH_3)_2.CO$, or as compounds of alcohol radicals with acid radicals, as $CH_3.C_2H_3O$ (acetone).

The following are the ketones best known. They correspond to the aldehydes $C_nH_{2n+1}.COH$, or to the fatty acids $C_nH_{2n+1}COOH$.

	NAME.	Formulæ.	Boiling Point.	
			° F.	° C.
	Dimethyl ketone (acetone)	$CO\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$		
	Methyl ethyl ketone	$CO\left\{\begin{matrix}CH_3\\C_2H_5\end{matrix}\right.$		
Isomeric.	Methyl-isopropyl ketone	$CO\left\{\begin{matrix}CH_3\\CH(CH_3)_2\end{matrix}\right.$	199·4	93
	Methyl propyl ketone	$CO\left\{\begin{matrix}CH_3\\C_3H_7\end{matrix}\right.$	213·8	101
	Diethyl ketone (propione)	$CO\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$	212·0	100
Iso-meric.	Methyl butyl ketone	$CO\left\{\begin{matrix}CH_3\\C_4H_9\end{matrix}\right.$	260·6	127
	Ethyl propyl ketone	$CO\left\{\begin{matrix}C_2H_5\\C_3H_7\end{matrix}\right.$	262·4	128
Iso-meric.	Methyl-isoamyl ketone..	$CO\left\{\begin{matrix}CH_3\\C_5H_{11}\end{matrix}\right.$	311·0	155
	Dipropyl ketone (butyrone)	$CO\left\{\begin{matrix}C_3H_7\\C_3H_7\end{matrix}\right.$	291·2	144

Acetone, the ketone of acetic acid, is the only one of these bodies that has received particular attention. It is a colorless, limpid liquid, having a specific gravity of 0·792, and a vapor density (air = 1) of 2·022. It burns with a bright flame, and mixes with water, alcohol, and ether in all proportions.

We may here note the general preparation and reactions of the ketones of the $CO(C_nH_{n2+1})_2$ group.

Preparation.—1. By the action of carbonic oxide on the sodium organo-metallic compounds, such as sodium ethide. Thus:—

$$\begin{array}{ccccccccc} 2NaC_2H_5 & + & CO & = & Na_2 & + & CO(C_2H_5)_2. \\ \text{Sodium ethyl} & + & \text{Carbonic oxide} & = & \text{Sodium} & + & \text{Diethyl ketone.} \end{array}$$

2. By the action of the acid chlorides on the zinc organo-metallic compounds. Thus:—

$$\begin{array}{ccccccc} Zn(CH_3)_2 & + & 2CO.CH_3Cl & = & ZnCl_2 & + & 2[CO(CH_3)_2]. \\ \text{Zinc methide} & + & \text{Acetic chloride} & = & \text{Zinc chloride} & + & \text{Dimethyl ketone.} \end{array}$$

3. By the oxidation of the secondary monohydric alcohols. Thus:—

$$\begin{array}{ccccc} CH(CH_3)_2OH + O & = & H_2O & + & CO(CH_3)_2. \\ \text{Isopropyl alcohol} & = & \text{Water} & + & \text{Dimethyl ketone.} \end{array}$$

4. By the distillation of the calcium salts of the fatty or other monohydric acids, or mixtures thereof. Thus:—

$$\begin{array}{cccccc} (\alpha.) & Ca(C_2H_3O_2)_2 & = & CaCO_3 & + & CO(CH_3)_2. \\ & \text{Calcium acetate} & = & \text{Calcium carbonate} & + & \text{Acetone.} \end{array}$$

$$\begin{array}{cccccccc} (\beta.) & Ca(C_5H_9O_2)_2 & + & Ca(C_2H_3O)_2 & = & 2CaCO_3 & + & 2(CO.CH_3.C_4H_9). \\ & \text{Calcium valerate} & + & \text{Calcium acetate} & = & \text{Calcium carbonate} & + & \text{Methyl-butyl ketone.} \end{array}$$

Ketones *differ* from aldehydes as follows:—

1. That whereas aldehydes form acids by spontaneous oxidation, ketones do not.

2. That whereas aldehydes, by reduction with nascent hydrogen, yield *primary* alcohols, ketones yield *secondary* alcohols.

3. That whereas aldehydes reduce an ammoniacal solution of argentic oxide, ketones do not.

Ketones *resemble* aldehydes by forming crystalline compounds with hydric-sodic or hydric-potassic sulphate, from which the ketone may be afterwards liberated by distillation with an alkali.

With hydrocyanic acid the ketones form cyanides, which, when digested with hydrochloric acid and water, form acids of the lactic series.

Acetone. Dimethyl Ketone. $CO(CH_3)_2$.

Preparation.—Acetone can be prepared by any of the above general methods, but it is best prepared by the dry distillation of calcium or lead acetate. The crude distillate is saturated with potassium carbonate, and rectified over calcium chloride in a water-bath.

Properties.—Acetone is a colorless liquid, possessing a peculiar odor. It has a specific gravity of 0·795, and boils at 55·3° C. (131·5° F.). It is miscible in all proportions with water, alcohol, and ether. It is used in the arts as a solvent.

CHAPTER XXVIII.

THE ALKALOIDS. AMMONIA DERIVATIVES.

THE AMMONIA DERIVATIVES—Amines—Amides — Imides — Nitriles — Phosphines—Arsines, etc.—Organo-Metallic Bodies—NATURAL ALKALOIDS—Vegetable and Animal.

THE alkaloids are a group of organic bodies, containing nitrogen, and capable of combining with acids to form salts. The solutions of the alkaloids have generally an alkaline reaction.

Many of the alkaloids can be prepared artificially, and from their method of preparation and their decompositions, their constitution is pretty well known. They may be considered as ammonia in which the hydrogen is replaced, wholly or in part, by a compound radical.

The constitution of the natural alkaloids is however, as yet very imperfectly understood. They are, however, probably, like the artificial alkaloids, derivatives of ammonia, but it is unknown by what radicals the hydrogen has been replaced.

I.—The Amines. Compound Ammonias.

An amine is an ammonia in which one or more of the hydrogen atoms have been replaced by one or more alcohol radicals (that is, a radical which, like CH_3, does not contain oxygen). The amines may be classified as follows:—

A. *Monamines.*—Bodies formed on the type of a single ammonia molecule (NH_3). Monamines are subdivided into three groups—

- α. Primary monamines, where one H only is replaced (NH_2R').
- β. Secondary monamines, where H_2 is replaced (NHR'_2).
- γ. Tertiary monamines, where H_3 is replaced (NR'_3).

B. *Diamines.*—Bodies formed on the type of a double ammonia molecule, N_2H_6.

C. *Triamines.*—Bodies formed on the type of a treble ammonia molecule, N_3H_9.

D. *Tetramines.*—Bodies formed on the type of a quadruple ammonia molecule, N_4H_{12}.

A. **Monamines.**—*Organic bases formed on the type of a single ammonia molecule.* The monamines may be primary, secondary, or tertiary.

α. *Primary monamines*, that is, *ammonias where one hydrogen atom has* *een replaced by one compound hydrocarbon radical. Example:*—ethyl-mine, $NH_2(C_2H_5)$.

Preparation.—1. By the action of the caustic alkalies on cyanates f the alcohol radicals:—

$$C_2H_5.CNO + 2KHO = NH_2.C_2H_5 + K_2CO_3.$$

Ethylic cyanate + Potassic hydrate = Ethyl-amine + Potassic carbonate.

2. By the action of the iodides or other haloid compounds of the ıcohol radicals on ammonia, and the subsequent decomposition of the ɔmpound formed by potassic hydrate:—

$$(\alpha.)\quad C_2H_5I + NH_3 = NH_2.C_2H_5HI.$$

Ethylic iodide + Ammonia = Ethylammonic iodide.

$$(\beta.)\quad NH_2(C_2H_5)HI + KHO = NH_2(C_2H_5) + KI + H_2O.$$

Ethylammonic iodide + Potassic hydrate = Ethylamine + Potassic iodide + Water.

[This process is also available for the preparation of secondary and ·rtiary monamines.]

3. By the action of reducing agents on certain nitro derivatives of ıe hydrocarbons:—

$$C_6H_5(NO_2) + 3H_2 = NH_2(C_6H_5) + 2H_2O.$$

Nitro-benzene + Hydrogen = Aniline (phenylamine) + Water.

β. Secondary monamines, that is, *ammonias* (NH_3), *where two hy-·ogen atoms are replaced by two compound radicals, the same or different. ˈxample:* Diethylamine, $NH(C_2H_5)_2$.

Preparation.—By the action of a haloid compound of an alcohol dical on a *primary* monamine (the alcohol radical being the same or fferent to that contained in the monamine), and the subsequent action ı the product of potassic hydrate:—

$$(C_2H_5)I + NH_2(C_2H_5) = NH(C_2H_5)_2 + HI.$$

Ethylic iodide + Ethylamine = Diethylamine + Hydriodic acid.

(γ.) *Tertiary monamines*, that is, *ammonias* (NH_3), *where three hydro-n atoms are replaced by three compound radicals, the same or different. xample:* Triethylamine, $(NC_2H_5)_3$.

Preparation.—By acting in a similar manner to that described above ith ethylic iodide on a *secondary* monamine:—

$$(C_2H_5)I + NH(C_2H_5)_2 = N(C_2H_5)_3 + HI.$$

Ethylic iodide + Diethylamine = Triethylamine + Hydriodic acid.

[NOTE.—In practice, when we act on ammonia with ethylic iodide, l these compounds are formed in varying proportions. They cannot separated by fractional distillation.]

Properties of the Amines.—The amines are, with few exceptions, ·sic compounds. They are alkaline, and possess an ammoniacal and ·h-like odor. They precipitate many metallic salts, and combine rectly with acids to form crystalline salts. Their chlorides form with platinum chloride the double salt analogous to ammonium-platinic chloride. The salts of the amines are decomposed by the action of alkalies just like ammonia salts.

Primary amines are converted by the action of *nitrous* acid into the corresponding alcohol, the *secondary* amines being converted under similar conditions into nitroso compounds.

$$NH(C_2H_5)_2 + H.NO_2 = \underset{\text{Nitroso-diethylamine}}{N(C_2H_5)_2.NO} + H_2O.$$

The *tertiary* amines are not affected by nitrous acid, but they combine with the alcoholic iodides, giving rise to an iodide of a compound ammonia which is not decomposed by potassic hydrate, and which moist silver oxide converts into hydroxides.

The following is a list of the chief monamines:—

Names.	Formulæ.	Specific Gravity of Liquid.	Boiling point.		Properties.
			° F.	° C.	
Methylamine ..	$NH_2(CH_3)$	1·08			A gas, alkaline, and of ammoniacal odor. Liquefied at —0·4° F. (—18° C.). One vol. of water at 53·6° (12° C.) dissolves 1,040 vols. of gas. Inflammable, and burns with a yellow flame. It occurs in herring brine, and is a product of the action of H on HCN.
Dimethylamine..	$NH(CH_3)_2$				A colorless gas, boiling at 46·4° F. (8° C.). Smells of NH_3 Isomeric with Ethylamine.
Trimethylamine ..	$N(CH_3)_3$				A colorless gas, liquefying at 48·7° F. (9·3 C.). Smells of ammonia and fish brine. Isomeric with Propylamine.
Tetramethyl-ammonic hydrate.	$N(CH_3)_4(OH)$				When heated it yields trimethylamine and methyl alcohol.
Ethylamine ..	$NH_2(C_2H_5)$	0·6964 at 8° C.	66·2	19·0	Specific gravity of vapor, 1·57. Ammoniacal odor. Alkaline reaction. Forms salts with acids. Fumes with HCl. Like ammonia, precipitates metallic salts, dissolves AgCl, and produces a blue ppt. with copper salts. Vapor inflammable. Decomposed by HNO_2 into N and ethyl nitrite.
Diethylamine ..	$NH(C_2H_5)_2$		135·5	57·5	A colorless alkaline liquid, soluble in water; forms salts with acids.
Triethylamine ..	$N(C_2H_5)_3$		195·8	91·0	A colorless alkaline liquid. Forms crystalline salts with acids.

Names.	Formulæ.	Specific Gravity of Liquid.	Boiling Point.		Properties.
			° F.	° C.	
trethyl-ammonic hydrate	$N(C_2H_5)_4(OH)$				Crystalline. The crystals decomposed by heat into methylamine, water, and ethylene. The solution is colorless, alkaline and bitter. Closely related to potassic hydrate.
——					
nylamine ..	$NH_2(C_5H_{11})$	0·7503 at 18° C.	199·4	93·0	A colorless liquid, alkaline, having an ammoniacal smell.
amylamine ..	$NH(C_5H_{11})_2$		338·0	170·0	An alkaline liquid.
iamylamine ..	$N(C_5H_{11})_3$		494·6	257·0	A colorless liquid; the salts are sparingly soluble in water.
tramyl-ammonic hydrate	$N(C_5H_{11})_4(OH)$				A solid crystalline body; when heated it yields triamylamine, amylene, and water. It is not very soluble in water.
——					
tylamine ..	$NH_2(C_4H_9)$				
butylamine ..	$NH(C_4H_9)_2$				
ibutylamine ..	$N(C_4H_9)_3)$				
trabutyl-ammonic hydrate	$N(C_4H_9)_4(HO)$				
lylamine ..	$NH_2(C_3H_5)$				
allylamine ..	$NH(C_3H_5)_2$				
iallylamine ..	$N(C_3H_5)_3$				
tra-allyl-ammonic hydrate	$N(C_3H_5)_4(OH)$				
——					
thyl-ethyla-nine	$NH(CH_3)(C_2H_5)$				
thyl-ethyl-phenylamine	$N(CH_3)(C_2H_5)(C_6H_5)$				
yl-amylamine	$NH(C_2H_5)(C_5H_{11})$				
——					
nzylamine ..	$NH_2(C_7H_7)$		359·6	182·0	A colorless liquid. It absorbs CO_2 and fumes with HCl.
benzylamine ..	$NH(C_7H_7)_2$				
benzylamine .	$N(C_7H_7)_3$				
——					
lylamine ..	$NH_2(C_8H_9)$		384.8	196·0	Oily liquids, soluble in alcohol and ether, insoluble in water.
ylylamine ..	$NH(C_8H_9)_2$				
xylylamine ..	$N(C_8H_9)_3$				
——					
mylamine ..	$NH_2(C_{10}H_{13})$		536·0	280·0	Oily liquids.
ymylamine ..	$NH(C_{10}H_{13})_2$		572·0	300·0	
cymylamine	$N(C_{10}H_{13})_3$.				A crystalline solid. Melts at 177·8° F. (81° C.).
——					
phthalidine ..	$NH_2(C_{10}H_7)$				A crystalline solid. Prepared by the action of NH_4HS on an alcoholic solution of nitronaphthalene. Forms salts.
iline (phenylanine)	$NH_2(C_6H_5)$	1·028	359·6	182·0	

Names.	Formulæ.	Specific Gravity of liquid.	Boiling point.		Properties.
			° F.	° C.	
Toluidine.. .. (tolylamine; amidotoluene)	$NH_2(C_6H_4Me)$ or $NH_2(C_7H_7)$				Exists in three forms; as *para-toluidine*, a crystalline solid, melting at 45° C.: *ortho-toluidine*, a liquid, Sp. Gr. 0·998, boiling at 197° C., becoming rose colored on exposure to air; and *meta-toluidine*, a crystalline solid melting at 57° C.
Conine	$NH(C_8H_{14})''$				
Piperidine	$NH(C_5H_{10})''$				
Pyrrol	$N(C_4H_5)$	1·077	271·4	133·0	Prepared from animal oils. A colorless liquid, turns a piece of fir wood moistened with HCl purple.
Pyridine	$N(C_5H_5)'''$		242·6	117·0	Prepared from coal tar naphtha, and by heating amyl nitrate with phosphoric anhydride $C_5H_{11}NO_3-3H_2O=N(C_5H_5)$
Picoline (paraniline)	$N(C_6H_7)'''$	0·955	271·4	133·0	A liquid prepared from coal tar naphtha.
Lutidine	$N(C_7H_9)'''$		309·2	154·0	Do.
Collidine (xylidine)	$N(C_8H_{11})'''$		419.0	215·0	Do.
Chinoline	$N(C_9H_7)$	1·081	455·0	235·0	By distilling quinine, etc., with a strong solution of potassic hydrate. A colorless oily liquid forming salts with acids.
Parvoline (cumidine)	$N(C_9H_{13})'''$		370·4	188·0	A liquid prepared from coal tar naphtha.
Cymidine (coridine)	$N(C_{10}H_{15})'''$		482·0	250·0	
Rubidine	$N(C_{11}H_{17})'''$		446·0	230·0	
Viridine	$N(C_{12}H_{19})'''$		483·8	251·0	

(B.) **Diamines.**—*Organic bases formed on the type of a double ammonia molecule* (N_2H_6).

Preparation.—By the action of a haloid salt of a diatomic alcohol radical (as ethene (ethylene), C_2H_4, etc.), on ammonia. Thus:—

$$\underset{\text{Ammonia}}{2NH_3} + \underset{\text{Ethylene dibromide}}{(C_2H_4)''Br_2} = \underset{\text{Ethylene diamine}}{N_2H_4(C_2H_4)''} + \underset{\text{Hydrobromic acid.}}{2HBr.}$$

That is, $N_2H_4(C_2H_4)''$ represents a double ammonia molecule (N_2H_6), where two atoms of hydrogen have been replaced by the diatomic radical $(C_2H_4)''$.

Also diethene-diamine ($N_2H_2(C_2H_4)_2$) and triethene-diamine ($N_2(C_2H_4)_3$) can be produced by the action of ethene dibromide on ammonia.

The diamines unite directly with water to form ammonia hydrates:

$$N_2H_4.(C_2H_4)'' + H_2O = (C_2H_4)''N_2H_6O.$$

The following table represents some of the diamines:—

Name.	Formula.	Boiling point.		Properties.
		° F.	° C.	
Ethylene diamine.. ..	$N_2H_4(C_2H_4)''$	242·6	117·0	An oily liquid.
Urea	$N_2H_4(CO)''$			
Sulphur-urea	$N_2H_4(CS)''$			
Ethyl-urea	$N_2H_3(C_2H_5)'(CO)''$			
Sulpho-phenyl-urea ..	$N_2H_3(C_6H_5)'(CS)''$			

(C.) **Triamines.**—*Organic bases formed on the type of a treble ammonia molecule* (N_3H_9).

To this class belong many of the bases of the aniline colors, such as *rosaniline*, etc.

There are certain other amines to which mere reference must suffice, it being impossible to classify them:—

Name.	Formulæ.	Sp. Gr.	Properties.
Furfurine ..	$C_{15}H_{12}N_2O_3$		Prepared by boiling *furfuramide*, a body formed by the action of ammonia on a solution of furfurol ($C_5H_4O_2$) in potassic hydrate. A powerful base soluble in boiling water (1 in 135), in alcohol, and in ether. Solutions alkaline; salts bitter.
Benzoline; (amarine)	$C_{21}H_{18}N_2$		By the action of potassic hydrate on hydrobenzamide (C_7H_6O). A solid substance insoluble in water.
Thialdine ..	$C_6H_{13}NS_2$	1·191	Forms solid, highly refracting crystals. It is volatile, and yields salts with acids.

Aniline ($C_6H_7N = 93$).

Specific Gravity, 1·028; *Freezing point*, 17·6° F. (—8° C.); *Boiling point*, 359·6° F. (182° C.); *Molecular volume*, $\boxed{}\boxed{}$.

Origin of Name.—From the indigo plant, *Indigofera anil.*

Synonyms.—*Phenylamine* (regarding it as an ammonia derivative); *Phenylia*; *Amido-benzene.*

Constitution.—Aniline may be regarded either (1) as an ammonia derivative, where one of hydrogen is displaced by one of phenyl (C_6H_5):—hence called *phenylamine*, $NH_2(C_6H_5)'$; or (2) as an amido-derivative of benzoic acid, hence called *amido-benzene*, $C_6H_5(NH_2)$.

For the following reasons we are led to regard aniline as an ammonia:—

(*a.*) *Its behaviour with ethylic iodide.*—Thus it forms successively ethyl-phenyl-, diethyl-phenyl-, and triethyl-phenyl-ammonic iodide, the two former yielding—

$$\textit{Ethyl-phenyl amine}\ \left.\begin{matrix}C_2H_5\\ C_6H_7\\ H\end{matrix}\right\}N\text{; and }\textit{Diethyl-phenyl amine}\ \left.\begin{matrix}C_2H_5\\ C_2H_5\\ C_6H_7\end{matrix}\right\}N$$

respectively, when treated with potassic hydrate; the last yielding triethyl-phenylammonic hydrate when treated with water and argentic oxide.

This reaction corresponds to that of amines, as already explained (page 750).

(*β.*) As potassic hydrate separates NH_3 from ammonic salts, so it separates aniline (C_6H_7N) from aniline salts.

(*γ.*) By heating together phenic acid and ammonia in an hermetically sealed tube, aniline is formed by the substitution of phenyl (C_6H_5) for hydrogen.

(*δ.*) The salts of aniline correspond to the salts of ammonia.

Preparation.—(1.) By distilling powdered indigo with a saturated solution of potassic hydrate:—

$$\underset{\text{Indigo}}{C_8H_5NO} + \underset{\text{Potash}}{4KHO} + \underset{\text{Water}}{H_2O} = \underset{\text{Hydrogen}}{2H_2} + \underset{\text{Potassic carbonate}}{2K_2CO_3} + \underset{\text{Aniline.}}{C_6H_7N.}$$

(2.) By heating together ammonia and phenol for two or three weeks in sealed tubes (Laurent)—

$$\underset{\text{Phenol}}{C_6H_5(OH)} + \underset{\text{Ammonia}}{NH_3} = \underset{\text{Water}}{H_2O} + \underset{\text{Aniline.}}{C_6H_5(NH_2)}$$

(3.) By the action of reducing agents on nitro-benzene; such as,—

(*a.*) *Sulphuretted hydrogen* (Zinin)—

$$\underset{\text{Nitro-benzene}}{C_6H_5(NO_2)} + \underset{\text{Sulphuretted hydrogen}}{3H_2S} = \underset{\text{Water}}{2H_2O} + \underset{\text{Sulphur}}{S_3} + \underset{\text{Aniline.}}{C_6H_7N.}$$

(*β.*) *Ferrous acetate* (Béchamp)—

(*γ.*) *Dilute sulphuric acid and zinc* (*i.e., nascent hydrogen*)—

$$\underset{\text{Nitro-benzene}}{C_6H_5(NO_2)} + \underset{\text{Hydrogen}}{3H_2} = \underset{\text{Water}}{2H_2O} + \underset{\text{Aniline.}}{C_6H_7N.}$$

[In the commercial manufacture of aniline, nitro-benzene is heated in a retort with glacial acetic acid and iron filings, when the aniline distils over, together with water, which floats upon the aniline. It is then drawn off from the water, any acetate present being decomposed with an alkali, and redistilled. All the aniline of commerce contains toluidine, since commercial benzene always contains toluene.]

Aniline is found amongst the products of the distillation of coal and other organic matters.

Properties.—(*a.*) *Sensible.* Aniline when pure is a colorless oily liquid, but on exposure to light and air turns brown. It has a peculiar odor and a burning taste. It is an active poison.

(β.) *Physical.* Specific gravity, 1·028. It freezes at 17·6° F. (—8° C.), forming a crystalline mass. It boils at 359·6° F. (182° C.). It is slightly soluble in water (forming, possibly, a hydrate), and is very soluble in alcohol and ether.

(γ.) *Chemical.* The aqueous solution has an extremely weak alkaline reaction, not sufficient, however, to blue red litmus paper. Its vapor forms white fumes with hydrochloric acid. By contact with air it becomes of a dark color and of resinous consistency. By the action upon it of oxidizing agents, the various aniline colors are formed. With the haloids (but not by their direct union) it forms substitution products, as chlor- or brom-aniline (C_6H_6ClN), dichlor- or dibrom-aniline ($C_6H_5Cl_2N$), and trichlor- or tribrom-aniline ($C_6H_4Cl_3N$). The first two of these haloid substitution compounds are bases, and form salts; but the last compound, *i.e.* where the substitution is complete, is neutral. Aniline is a powerful organic base, and with acids forms crystalline salts.

Numerous other substitution products of aniline have been prepared, as, *e.g.*, *nitraniline*, $C_6H_6(NO_2)N$, a body existing in two modifications; *dinitraniline*, $C_6H_5(NO_2)_2N$; *diphenylamine*, $NH(C_6H_5)_2$, etc. With cyanogen it forms the compound *cyan-aniline* $(C_6H_7N)_2Cy_2$.

When nitrous acid is passed (α) into aniline, *phenol*, nitrogen, and water are evolved; but when the acid is passed through (β) an alcoholic solution of aniline, *azodiphenyl-diamine* and water are formed. (γ) If azodiphenyl-diamine be treated with nitrous acid, an explosive body, *diazo-diphenylamine*, is produced.

These several reactions may be shown as follows:

(α.) $C_6H_7N + HNO_2 = C_6H_6O + H_2O + N_2.$

Aniline + Nitrous acid = Phenol + Water + Nitrogen.

(β.) $2C_6H_7N + HNO_2 = C_{12}H_{11}N_3 + 2H_2O.$

Aniline + Nitrous acid = Azodiphenyl-diamine + Water.

(γ.) $C_{12}H_{11}N_3 + NO_3 = C_{12}N_8H_4 + 2H_2O.$

Azodiphenyl-diamine + Nitrous acid = Diazo-diphenyl-diamine + Water.

With an *alkaline hypochlorite* aniline forms a violet (mauve). With *chromic acid* it gives a bluish-black precipitate. Heated with *mercuric chloride* it forms magenta.

Uses.—For the manufacture of dyes.

Toluidine (C_7H_9N). This base is homologous with aniline. It is found in three states—(1) as a *solid* (*paratoluidine*), melting at 113° F. (45° C.), and boiling at 401° F. (205° C.); (2), as *a liquid* (*orthotoluidine*), boiling at 386·6° F. (197° C.); specific gravity, 0·998°; and (3), as a *second solid* (*metatoluidine*), melting at 134·6° F. (57° C.), and boiling at 464° F. (240° C.).

Aniline Dyes.

Aniline Purple, or Mauve.—This dye is prepared by mixing a cold solution of aniline sulphate with a cold solution of acid potassic dichromate. The mixture, after being well stirred, is left for twelve hours, when a black precipitate is formed. This precipitate is collected and washed, then digested with light coal tar oil to dissolve out the tarry matter which has been formed. The residue, after being dried, is digested with alcohol, which dissolves out the colouring matter. The alcohol is distilled off, and the aniline purple remains.

Aniline purple is a salt, generally the sulphate, of the base *mauveine*, $C_{27}H_{24}N_4$; it is insoluble in water, in ether, and in benzene, but freely soluble in alcohol and in acetic acid.

Aniline Red, or Rosaniline: Magenta.—*Preparation.* By the action on aniline of various oxidizing agents, such as stannic chloride, arsenic acid, mercuric chloride, etc. One of the best commercial processes is its oxidation with arsenic acid. Twelve parts of the dry arsenic acid of commerce is mixed with ten parts of aniline. The mixture is heated to 120°—140° C. for about six hours. The brown mass thus produced is dissolved in boiling water, and the coloring matter precipitated free from arsenic by the addition of soda. The precipitate is collected, washed and dissolved in acetic acid.

Aniline red is a salt of base *rosaniline*, $C_{20}H_{19}N_3$. This base is a triamine capable of combining with one or three atoms of an acid; also three of its hydrogen atoms may be replaced by alcohol radicals, such as methyl, ethyl, or phenyl, producing other dyes. It has been shown that *pure* aniline is incapable of furnishing aniline red, and that the aniline used has to contain toluidine.

Rosaniline is nearly insoluble in water, but is soluble in alcohol. The salts (mono-acid) exhibit by reflected light the lustrous green of the wings of the rose beetle; they are moderately soluble in water, and very soluble in alcohol. The salts chiefly used in dyeing silk and wool are the acetate and hydrochlorate.

Triethyl-Rosaniline: *Hofmann's Violet*, $C_{20}H_{19}(C_2H_5)_3N_3$.—*Preparation.* By heating a mixture of one part of rosaniline, two parts of iodide of ethyl, and two parts of alcohol to 100° C. for three or four hours in a closed vessel. The resulting mass is then dissolved in alcohol and treated with caustic potash, whereby the methyl rosaniline is precipitated, and potassic iodide remains in solution. [From the solution the iodine is recovered.] The precipitate is washed, and then dissolved in alcohol containing acetic acid.

Triphenyl Rosaniline: *Aniline Blue*, $C_{20}H_{16}(C_6H_5)_3N_3$.—*Preparation.* By heating a salt of rosaniline with excess of aniline—

$$C_{20}H_{19}N_3,HCl+3(C_6H_5,NH_2)=C_{20}H_{16}(C_6H_5)_3N_3,HCl+3NH_3.$$

Properties.—Hydrochlorate of triphenyl rosaniline is a crystalline powder, perfectly insoluble in water and in ether, but soluble in alcohol, forming a deep blue solution.

Aniline Brown.—*Preparation.* By heating aniline blue with four parts of aniline hydrochlorate to 240° C. for several hours.

It is soluble in water and in alcohol.

Aniline Green.—(*α.*) *Aldehyde Green. Preparation.* By adding aldehyde to a solution of magenta and sulphuric acid, and then treating the product with sodium thiosulphate.

(*β.*) *Iodine Green.*—By the action of methyl- or ethyl-iodide on aniline violets.

Aniline Yellow, or Chrysaniline, $C_{20}H_{17}N_3$.—This is obtained as a bye-product in the manufacture of rosaniline. It is a yellow amorphous powder, and forms two series of salts, mono-acid and di-acid. The nitrate is insoluble in water. Chrysaniline and its salts dye silk a golden yellow color.

Aniline Black.—This color is produced *on calico* by printing with a mixture of aniline, chlorate of potassium, and sulphide of copper. Aniline black thus produced has a very rich and deep color. It is very fast, quite insoluble in water, alkalies, and acids.

Amides; Imides; Alkalamides; Nitriles.

An amide is a compound of amidogen (NH_2) and an acid radical.

We may regard the amides either as :—

(1.) Derivatives of ammonia; or as

(2.) Derivatives of organic acids.

1. *As derivatives of ammonia;* that is, an *amide* may be regarded as an ammonia where one or more atoms of hydrogen are replaced by *an acid radical, i.e.*, a radical containing oxygen (such as C_2H_3O, the radical of acetic acid).

[N.B.—An *amine* is regarded as an ammonia where one or more atoms of hydrogen are replaced by *an alcohol or hydrocarbon radical, i.e.*, a radical containing no oxygen (as CH_3, methyl, etc.)].

Thus the amides may be obtained from their ammonium salts by the abstraction of water, and may be converted into their ammonium salts by the assimilation of water.

Thus by driving off water by heat from ammonium acetate or ammonium oxalate we obtain acetamide and oxamide respectively. Thus :—

$$\underset{\substack{\text{Ammonium}\\ \text{acetate}}}{NH_4(C_2H_3O_2)} \underset{\text{—}}{—} \underset{\text{Water}}{H_2O} \underset{=}{=} \underset{\text{Acetamide}}{NH_2(C_2H_3O)}\,;\; \underset{\substack{\text{Ammonium}\\ \text{oxalate}}}{(NH_4)_2(C_2O_4)} \underset{\text{—}}{—} \underset{\text{Water}}{(H_2O)_2} \underset{=}{=} \underset{\text{Oxamide.}}{(NH_2)_2C_2O_2.}$$

and conversely, by heating acetamide and oxamide with water, we reproduce from them ammonium acetate and ammonium oxalate.

2. *As derivatives of acids;* that is, an amide may be regarded as an acid where the group (HO) is replaced by amidogen (NH_2).

By acting with ammonia on a chlor-acid, as acetylic chloride (which is acetic acid, $C_2H_3O(HO)$, where Cl has replaced the group (HO)), we obtain acetamide. Thus :—

$$\underset{\text{Acetylic chloride}}{C_2H_3O.Cl} \; + \; \underset{\text{Ammonia}}{NH_3} \; = \; \underset{\text{Acetamide}}{C_2H_3O(NH_2)} \; + \; \underset{\text{Hydrochloric acid.}}{HCl.}$$

Thus it would appear that we may formulate the amides in two ways. For example: acetamide and oxamide.

(1.) As *ammonia derivatives*, they may be stated as follows :—

$$N\left\{\begin{array}{l} H \\ H \\ (C_2H_3O) \end{array}\right. = \underset{\text{Acetamide;}}{NH_2(C_2H_3O)} \; ; \; N_2\left\{\begin{array}{l} H_2 \\ H_2 \\ (C_2O_2)'' \end{array}\right. = \underset{\text{Oxamide.}}{(NH_2)_2(C_2O_2).}$$

(2.) As *acid derivatives* (of acetic acid, $CH_3CO(HO)$, and of oxalic acid, $C_2O_2(HO)_2$ respectively), as follows :—

$$\underset{\text{Acetamide}}{C_2H_3O(NH_2),} \quad \underset{\text{or}}{\text{or}} \quad \underset{\text{Oxamide.}}{C_2O_2(NH_2)_2.}$$

An imide is an ammonia derivative where two of the three hydrogen atoms are replaced by one molecule of a bivalent acid radical.

An imide, therefore, is a compound of imidogen $(NH)''$, *and a bivalent acid radical.* Thus :—

$$(NH)''(C_4H_4O_2)'' = \text{Succinimide.}$$

An alkalamide may be regarded as an ammonia derivative where the hydrogen is partly replaced by an alcohol (positive) radical, and partly by an acid radical: *e.g.*—

$$\text{Ethyl acetamide} = NH\,(C_2H_5)\,(C_2H_3O).$$

There are no primary alkalamides, inasmuch as two atoms of hydrogen in every case must be substituted.

We append tables of the chief amides of monatomic, diatomic, and triatomic acids.

I.—Amides of Monatomic Acids.

	Name.	Formulæ.	Acid from which derived	Properties.
Primary monamides ..	Acetamide	$NH_2(C_2H_5O)$	Acetic acid $C_2H_3O(OH)$	A white solid: melt at 172·4° F. (78° C.) and boils at 429·8 F. (221° C.).
	Benzamide	$NH_2(C_7H_5O)$	Benzoic acid $C_7H_5O(OH)$	A crystalline body melts at 239° F (115° C.), and volatilizes unchanged a 546·8° F. (286° C.)
Secondary monamides	Diacetamide Succinimide	$NH(C_2H_3)O_2$ $NH(C_4H_4O_2)''$		These containing trivalent acid radicals are called imides.
Secondary monamides or secondary *alkalamides*	Ethyl acetamide	$NH(C_2H_5)(C_2H_3O)$		
Tertiary monamides, or tertiary alkalamides	Ethyl diacetamide	$N(C_2H_5)(C_2H_3O)_2$		

II.—Amides of Diatomic Acids.

These are of three kinds—

(α.) *An acid amide* or *amic acid*, prepared from an acid ammonium salt by the abstraction of one water molecule, *e.g.*:—

$(NH_4)C_4H_5O_4$ (acid ammonic succinate) $-H_2O=(C_4H_4O_2)''(NH_2)(OH)$ (succinamic acid).

(β.) A *neutral monamide* or *imide*, prepared from an acid ammonium salt by the abstraction of two water molecules; *e.g.*:—

$(NH_4)C_4H_5O_4$ (acid ammonic succinate) $-(H_2O)_2=(C_4H_4O_2)''(NH)''$ (succinimide).

(γ.) A *neutral diamide* prepared from a neutral ammonium salt, by the abstraction of two water molecules; *e.g.*:—

$(NH_4)_2C_4H_4O_4$ (neutral ammonic succinate) $=(C_4H_4O_2)''(NH_2)_2$ (succinamide) $+2H_2O$.

Name.		Formulæ.	Properties.
mmonia salts of oxalic acid $C_2O_2(HO)_2$	Oxamic acid	$(C_2O_2)''(NH_2)(OH)$	White crystals; forms salts. If NH_2 be replaced by ethyl an acid oxamic ether is formed, but if the (OH) be replaced by ethyl, a neutral ether results.
	Oximide (?)	(?)	
	Oxamide ..	$(C_2O_2)''(NH_2)_2$	Formed also by the action of HCN on H_2O_2. Decomposed by heat into HCN and urea $C_2O_2(NH_2)_2=CO+CO_2+NH_3+CyH+CN_2H_4O$.
nmonia salts of succinic acid $C_4H_4O_2(OH)_2$	Succinamic acid ..	$(C_4H_4O_2)''(NH_2)(OH)$	
	Succinimide	$(C_4H_4O_2)''(NH)''$	
	Succinamide	$(C_4H_4O_2)''(NH_2)_2$	
nmonia salts of arbonic acid $CO(OH)_2$	Carbamic acid	$(CO)''(NH_2)(OH)$	Not known in a free state, but as an ammonia salt, which, when heated, forms ammonic carbonate and urea. It forms acid and neutral ethers.
	Carbimide ..	$(CO)''(NH)''$	Corresponds to cyanic acid.
	Carbamide ..	$(CO)''(NH_2)_2$	Corresponds to urea.

III.—Amides of the Triatomic Acids.

nmonia salts of malic acid $(C_4H_3O_2)'''(OH)_3$	Malamic acid	$(C_4H_3O_2)'''(NH_2)(OH)_2$	Not known in the free state.
	Malimide (?)	(?)	
	Malamide	$(C_4H_3O_2)'''(NH_2)_2(OH)$	Metameric with asparagin.
nmonia salts of citric acid $(C_6H_5O_4)'''(HO)_3$	Citramic acid	(?)	
	Citrimide	(?)	
	Citramide	$(C_6H_5O_4)'''(NH_2)_3$	

A nitrile is an ammonia derivative, where the three hydrogen atoms are placed by a trivalent radical.

Thus the cyanides of univalent alcohol radicals (alcohol cyanides or hydrocyanic ethers) may also be regarded as nitriles ; for example:—

Hydrocyanic acid	CHN	=	$(CH)N$	formonitrile.
Methylic cyanide	$CH_3.CN$	=	$(C_2H_3)'''N$	acetonitrile.
Ethylic cyanide	$C_2H_5.CN$	=	$(C_3H_5)'''N$	propionitrile.
Phenyl cyanide	$C_6H_5.CN$	=	$(C_7H_5)'''N$	benzonitrile.

The term "nitrile" is applied to all bodies similar to those obtained by the abstraction of two molecules of water from ammoniacal salts, and which are capable of being reconverted into the ammonia salt. Thus, if ammonic benzoate be distilled with anhydrous phosphoric acid, it furnishes benzonitrile,

$$\begin{array}{ccccc} (NH_4)C_7H_5O_2 & = & (C_7H_5)'''N & + & 2H_2O; \\ \text{Ammonic benzoate} & = & \text{Benzonitrile} & + & \text{Water.;} \end{array}$$

whilst ammonic benzoate is re-formed on boiling benzonitrile with dilute acids or alkalies.

By the action of fuming sulphuric acid, the nitriles yield sulpho-acids. Thus benzonitrile yields sulphobenzoic acid—

$$(C_6H_4(HSO_3)CO_2H).$$

By the action of potassic hydrate, the nitriles yield ammonia and a salt of the corresponding acid containing the same number of carbon atoms. Thus :—

$$\begin{array}{ccccccccc} (C_7H_5)'''N & + & KHO & + & H_2O & = & NH_3 & + & KC_7H_5O_2. \\ \text{Benzo-nitrile} & + & \text{Potassic hydrate} & + & \text{Water} & = & \text{Ammonia} & + & \text{Potassic benzoate.} \end{array}$$

This last reaction is important, inasmuch as certain cyanides or nitriles have been obtained, which, under the influence of hydrating agents, yield, instead of ammonia and the corresponding acid, an amine (or alcoholic ammonia) and formic acid. These are known as *isocyanides* or *carbamines*. For example : by the action of chloroform on aniline we obtain phenyl isocyanide, a body isomeric with benzonitrile. Thus :—

$$\begin{array}{ccccccc} C_6H_7N & + & CHCl_3 & = & 3HCl & + & C_7H_5N. \\ \text{Aniline} & + & \text{Chloroform} & = & \text{Hydrochloric acid} & + & \text{Phenyl isocyanide.} \end{array}$$

(α.) But *phenyl isocyanide*, when boiled with a dilute acid, yields formic acid and aniline. Thus :—

$$\begin{array}{ccccccc} C_7H_5N & + & 2H_2O & = & (C_6H_7)'''N & + & CH_2O_2. \\ \text{Phenyl isocyanide} & + & \text{Water} & = & \text{Aniline} & + & \text{Formic acid.} \end{array}$$

(β.) Whereas *benzonitrile* yields benzoic acid and ammonia. Thus :—

$$\begin{array}{ccccccc} C_7H_5N & + & 2H_2O & = & NH_3 & + & C_7H_6O_2. \\ \text{Bonzo-nitrile} & + & \text{Water} & = & \text{Ammonia} & + & \text{Benzoic acid.} \end{array}$$

The isocyanides are unaffected by alkalies, whilst the nitriles are easily decomposed.

Phosphines : Arsines : Stibines : Bismuthines.

Phosphorus, arsenic, and antimony, like nitrogen, form compounds with three atoms of hydrogen, viz., PH_3, AsH_3, SbH_3, which bodies also form compounds analogous to the amines (termed *phosphines*, *arsines*, etc.), excepting that in AsH_3 and in SbH_3, the replacement of the hydrogen is always complete.

Properties.—They are mostly liquids, having a very strong odor. Many of them are spontaneously inflammable. They have great affinity for oxygen and for the haloids, forming compounds in which the metal is quin-quivalent. Thus we have *stibethyl oxide*, $Sb^{v}(C_2H_5)_3O$; *stibethyl choride*, $Sb^{v}(C_2H_5)_3Cl_2$, etc. The tertiary compounds form, with ethylic or methylic iodide, compounds from which argentic oxide separates the hydrates ; thus—

$P(CH_3)_4HO$;	$P(C_2H_5)_4(HO)$;	$As(C_2H_5)_4(HO)$;	$Sb(C_5H_{11})_4(HO)$, etc.
Hydrate of tetramethyl phosphine ;	Hydrate of tetrethyl phosphine ;	Hydrate of tetrethyl arsine ;	Hydrate of tetramyl stibine.

Some of these compounds are stated in the following table :—

Name.	Formulæ.	Sp. Gr.	Boiling point.		Properties.
			° F.	° C.	
Phosphines.					
Methyl phosphine ..	$PH_2(CH_3)$		6·8	—14·0	
Dimethyl phosphine .	$PH(CH_3)_2$		77·0	25·0	
Trimethyl phosphine .	$P(CH_3)_3$		105·8	41·0	A colorless oil, very volatile.
Ethyl phosphine ..	$PH_2(C_2H_5)$		77·0	25·0	
Diethyl phosphine ..	$PH(C_2H_5)_2$		185·0	85·0	
Triethyl phosphine ..	$P(C_2H_5)_3$		261·5	127·5	Prepared by the action of phosphorous chloride (PCl_3) on zinc ethyl. A colorless oil, oxidizes in air, and explodes by heat.
Arsines.					
Trimethyl arsine ..	$As(CH_3)_3$		248·0	120·0	Prepared by the action of methylic iodide on an alloy of arsenic and sodium.
Triethyl arsine	$As(C_2H_5)_3$		284·0	140·0	Prepared by the action of ethylic iodide on an alloy of arsenic and sodium. A colorless liquid, having a very disagreeable odor.
Stibines.					
Trimethyl stibine ..	$Sb(CH_3)_3$				
Triethyl stibine .. .. (Stibethyl)	$Sb(C_2H_5)_3$		316·4	158·0	Prepared by the action of ethylic iodide on an alloy of antimony and potassium. Odor of onions ; combines powerfully with oxygen and the haloids.

Name.	Formulæ.	Sp.G.	Boiling point.		Properties.
			° F.	° C.	
Stibines (cont.)					
Triamyl stibine	$Sb(C_5H_{11})_3$				
Bismuthine.					
Triethyl bismuthine ..	$Bi(C_2H_5)_3$	1·82			Prepared by the action of ethylic iodide on an alloy of bismuth and potassium. A yellow, nauseous liquid.

Arsen-mono-methyl.—Kakodyl.

It will be convenient to examine these bodies here, which, however it must be specially noted, are not formed on the ammonia type.

Arsen-mono-methyl; $As(CH_3)$. This radical is not known in the free state. It forms compounds by combining with either two or four atoms of a univalent element or compound radical, or their equivalent. Thus it forms a *dichloride*, $As'''(CH_3)Cl_2$, which is a heavy, very poisonous liquid, and a *tetrachloride*, $As^{v}(CH_3)Cl_4$, a stable crystalline solid; *an oxide*, $As'''(CH_3)O$, a bibasic acid, called *arsen-methyllic acid*, $As^{v}(CH_3)O''(OH)_2$, *a sulphide*, $As'''(CH_3)S$, etc.

Kakodyl (Cacodyl); *Arsen-dimethyl*, $As'''_2(CH_3)_4$, or $As(CH_3)_2$. Boils at 338° F. (170° C.). Freezes at 42·8° F. (6° C.).

Preparation.—(*a.*) By distilling together potassic acetate and arsenious oxide, a spontaneously inflammable liquid is formed, called *alkarsin* (*Cadet's fuming liquid*):—

$$\underset{\substack{\text{Potassic}\\\text{acetate}}}{4KC_2H_3O_2} + \underset{\substack{\text{Arsenious}\\\text{oxide}}}{As_2O_3} = \underset{\text{Alkarsin}}{As_2(CH_3)_4O} + \underset{\substack{\text{Potassic}\\\text{carbonate}}}{2K_2CO_3} + \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{2CO_2}$$

(*β.*) This alkarsin combines with acids to form salts. Thus, by acting upon it with hydrochloric acid it forms a chloride, thus—

$$\underset{\text{Alkarsin}}{As_2(CH_3)_4O} + \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{2HCl} = \underset{\substack{\text{Chloride of}\\\text{alkarsin}}}{As_2(CH_3)_4Cl_2} + \underset{\text{Water.}}{H_2O.}$$

(*γ.*) By distilling this chloride of alkarsin with zinc, kakodyl [$As_2(CH_3)_4$] is obtained, together with zincic chloride, which latter product may be dissolved out with water.

Properties.—(*a.*) *Physical.* Kakodyl is a colorless, transparent, oily liquid, having a most offensive odor (κάκος bad). It is intensely poisonous. It boils at 338° F. (170° C.). At a heat below redness it resolves itself into arsenicum, methane, and ethene:—

$$\begin{array}{ccccccc} As_2(CH_3)_4 & = & As_2 & + & C_2H_4 & + & 2CH_4. \\ \text{Kakodyl} & = & \text{Arsenicum} & + & \text{Ethene (1 vol.)} & + & \text{Methane (2 vols.)} \end{array}$$

(β.) *Chemical.* Kakodyl catches fire spontaneously when poured into oxygen, air, or chlorine, and it also combines directly with sulphur. If the air in contact with it be limited, it forms kakodyl oxide, $As_2(CH_3)_4O$, and in the presence of water, *kakodylic acid.* The following are some of its compounds :—

Name.	Formulæ.	Preparation, Properties, &c.
Kakodyl oxide ..	$As_2'''(CH_3)_4O''$	*Preparation.* — By the slow oxidation of kakodyl. *Properties.*—A colorless, pungent, oily liquid. Boils at 120° C. It explodes when heated to 190·4° F. (88° C.), but does not fire in the air. It is insoluble in water, but is soluble in HCl, HBr and HI.
Kakodyl dioxide ..	$As_2(CH_3)_4O_2$	Decomposed by water into kakodyl oxide and kakodylic acid, $2(As_2CH_4O_2)+H_2O=As_2(CH_3)_4O+2As(CH_3)_2O(HO)$.
Kakodylic acid (alkargen)	$As^v(CH_3)_2O''(HO)$	*Preparation.*—By the slow oxidation of kakodyl in the presence of moisture. *Properties.*—Deliquescent crystals, soluble in water and in alcohol: reaction acid. It is very stable, and is not even affected by boiling nitro-hydrochloric acid. It is decomposed by dry HI. It combines with HCl. It is decomposed by PCl_5, forming a trichloride. It is not poisonous.
Kakodyl chloride .. (Arsen chloro-dimethide)	$As'''(CH_3)_2Cl$	*Preparation.*—By distilling alkarsin with HCl. *Properties.*—A colorless liquid, volatile at ordinary temperatures. Soluble in alcohol; insoluble in water or in ether. The vapor inflammable, and has a specific gravity of 4·56°.
Kakodyl trichloride	$As^v(CH_3)_2Cl_3$	*Preparation.*—By the action of PCl_5 on kakodylic acid.
Kakodyl iodide ..	$As(CH_3)_2I$	*Preparation.*—By distilling alkarsin with a strong solution of HI.
Kakodyl cyanide ..	$As(CH_3)_2Cy$	*Preparation.*—By distilling alkarsin with HCy, or by the action of oxide of kakodyl on cyanide of mercury. *Properties.*—Crystalline. . Melts at 91·4° F. (33° C.), and boils at 284° F. (140° C.). The vapor is very poisonous.
Kakodyl sulphide ..	$As_2(CH_3)_4S$	A liquid, boiling at about 248° F. (120° C.).
Kakodyl disulphide	$As_2(CH_3)_4S_2$	*Preparation.*—By the action of H_2S on kakodylic acid. *Properties.*—It yields salts of sulpho-kakodylic acid. $As^v(CH_3)_2S_2H$.

ORGANO-BORON, -SILICON, AND -METALLIC COMPOUNDS.

Boron, silicon, and certain metals, also combine with alcohol radicals, forming compounds built up on the ammonia type.

Organo-Boron Compounds.

These are compounds of boron with hydrocarbon radicals (as methyl ; CH_3), the boron being directly combined with the carbon :—

Name.	Formulæ.	Preparations, Properties, etc.
Boric methide ..	$B(CH_3)_3$	*Preparation.*—By adding an ethereal solution of zinc methide to boracic ether $2[B(C_2H_5)_3O_3]+3[Zn(CH_3)_2]=2[B(CH_3)_3]+3[Zn(C_2H_5)_2O_2]$ *Properties.*—A heavy, pungent gas; specific gravity 1·93 ; condenses at 50° F. (10° C.), under a pressure of four atmospheres; inflames spontaneously in air ; combines with ammonia to form ammonia boric methide $(NH_3,B(CH_3)_3)$.
Boric ethide .. (Triborethyl)	$B(C_2H_5)_3$	*Preparation.*—By adding an ethereal solution of zinc ethide to boracic ether. *Properties.* — A colorless liquid ; specific gravity, 0·696 ; boils at 203° F. (95° C.); inflames spontaneously in air, burning with a green flame. It combines with ammonia to form ammonia boric ethide, NH_3, $B(C_2H_5)_3$.

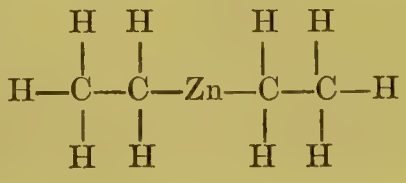
Organo-Silicon Compounds.

Compounds of silicon with hydrocarbon radicals, the silicon being directly combined with the carbon :—

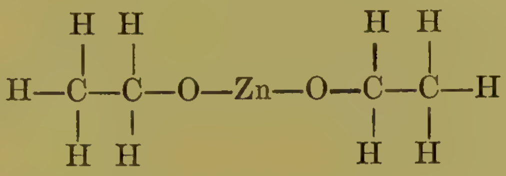
		Boiling point.		
		° F.	° C.	
Silicic methide ..	$Si(CH_3)_4$	86·9	30·5	*Preparation.*—By the action of zinc methide on silicic chloride.
Silicic ethide ..	$Si(C_2H_5)_4$	306·5	152·5	*Preparation.*—By the action of zinc ethide on silicic chloride.
Derivatives.				
Silicic methylate ..	$Si(CH_3)_4O_4$	249·8	121·0	
Silicic ethylate ..	$Si(C_2H_5)_4O_4$	331·7	166·5	

Organo-Metallic Bodies.

These are compounds of a metal and an alcohol radical, the metal being directly combined with the carbon of the radical. Thus zinc ethyl, $Zn(C_2H_5)_2$, is an organo-metallic body, and may be represented thus—



whilst zinc ethylate, $Zn(C_2H_5)_2O_2$, is not an organo-metallic body (the metal not being directly connected with the carbon of the radical), but is simply an organic body containing zinc, and may be represented thus—



$$\begin{array}{ccccccccccccccccc} & & H & & H & & & & & & & & H & & H & & \\ & & | & & | & & & & & & & & | & & | & & \\ H & - & C & - & C & - & O & - & Zn & - & O & - & C & - & C & - & H \\ & & | & & | & & & & & & & & | & & | & & \\ & & H & & H & & & & & & & & H & & H & & \end{array}$$

Preparation.—(1.) By the action of a metal on an iodide of the monad positive radical under the influence of heat, or sometimes of light—

$$2(C_2H_5)I \quad + \quad Zn_2 \quad = \quad Zn(C_2H_5)_2 \quad + \quad ZnI_2.$$

Ethylic iodide + Zinc = Zinc ethyl + Zinc iodide.

(2.) By the action of alloys of the metals with K or Na, on an iodide of the monad positive radicals—

$$2(C_2H_5)I \quad + \quad HgNa_2 \quad = \quad Hg''(C_2H_5)_2 \quad + \quad 2NaI.$$

Ethylic iodide + Sodium and mercury alloy = Mercuric ethide + Sodic iodide.

(3.) By the action of haloid salts of the metals (as $Sn^{iv}Cl_4$), on the zinc organo-metallic compounds:—

$$SnCl_4 \quad + \quad 2[Zn(C_2H_5)_2] \quad = \quad Sn(C_2H_5)_4 \quad + \quad 2ZnCl.$$

Stannic chloride + Zinc ethyl = Stannic ethyl + Zinc chloride.

(4.) By the displacement of one metal in an organo-metallic compound, by a second and more positive metal:—

$$Hg(C_5H_{11})_2 \quad + \quad Zn \quad = \quad Zn(C_5H_{11})_2 \quad + \quad Hg.$$

Mercuric amylide + Zinc = Zincic amylide + Mercury.

Some of these organo-metallic compounds are represented in the following table:—

Name.	Formulæ.		
Sodium ethide	$Na(C_2H_5)$	Corresponding to	NaCl
Zinc ethide	$Zn(C_2H_5)_2$	,,	$ZnCl_2$
,, methide	$Zn(CH_3)_2$	,,	$ZnCl_2$
,, amylide	$Zn(C_5H_{11})_2$	,,	$ZnCl_2$
Mercuric methide..	$Hg(CH_3)_2$	,,	$HgCl_2$
,, ethide	$Hg(C_2H_5)_2$	,,	$HgCl_2$
Stannous ethide	$Sn(C_2H_5)_2$	,,	$Sn''Cl_2$
Stannic ethide	$Sn(C_2H_5)_4$	,,	$Sn^{iv}Cl_4$
Plumbic ethide	$Pb(C_2H_5)_4$	,,	PbO_2
Aluminic methide	$Al_2(CH_3)_6$	,,	Al_2Cl_6

THE NATURAL ALKALOIDS.

Natural History.—The natural alkaloids are found in all parts of vegetables, and constitute the active ingredients of plants. They exist in combination with organic acids, which are often as peculiar to the plant as the alkaloid, *e.g.*, morphia, etc., with meconic acid; quinine, etc., with kinic acid; strychnia with igasuric acid; atropine with malic acid, etc.

A few alkaloids are found in the animal kingdom, *e.g.*, urea, kreatine, etc.

Preparation.—The *fixed alkaloids* are extracted from the plant, either by water, or by dilute sulphuric or hydrochloric acid. From this solution the alkaloid is precipitated by an alkali, or by an alkaline earth such as magnesia. The precipitate is then again dissolved in a dilute acid, decolorized with animal charcoal (which must be used very sparingly, owing to the great power it possesses of absorbing the alkaloids and their salts), and reprecipitated from the acid solution with an alkali. The precipitated alkaloid is then dissolved in boiling alcohol, the solution filtered, and the alkaloid crystallized from the solution.

The *volatile alkaloids* are prepared by distilling the plant in the presence of a very weak alkali. The distillate is always more or less ammoniacal from the decomposition of a portion of the alkaloid. After neutralization with oxalic or sulphuric acid, the distillate is evaporated to dryness. The residue is now treated with alcohol, and the upper layer of the mixture drawn off, filtered to separate extraneous matters, and again evaporated. This is treated with a mixture of ether and potassic hydrate, the latter for the purpose of combining with the acid, and the former to dissolve the alkaloid set free. The ethereal layer is then decanted and evaporated.

Properties.—(*a.*) *Sensible and Physical.* All the alkaloids are solid, except the three which contain no oxygen, viz., nicotine, conine, and sparteine. They all crystallize easily from alcoholic solutions, except quinine, which crystallizes with difficulty, and quinoidine, which is not crystalline. None of them, except the three liquid alkaloids mentioned, have any odor. Their taste is generally more or less bitter. Their physiological actions are very energetic. In treating cases of poisoning occurring from their exhibition, we may say, generally, that the stomach-pump and emetics are indicated, as well as astringent liquids, such as strong tea, etc. Tannic acid precipitates most alkaloids from their aqueous solution.

Action of Heat.—Conine, nicotine, sparteine, theine, and caffeine sublime by heat unchanged: piperine, when heated, yields piperdine. All the alkaloids are decomposed (ammoniacal compounds being formed), if the heat applied be sufficient.

Action of Light.—The alkaloids generally have a powerful influence on a polarized beam, some rotating the beam to the right and others to the left.

Quinine solutions are remarkable for their fluorescence.

Action of Electricity.—The salts of the alkaloids (like other salts) liberate the base at the platinode of the battery.

Action of Solvents.—*Water.* The alkaloids generally are but slightly soluble in water, nicotine being one of the most soluble. *Alcohol* dissolves them all, but in varying proportions; thus cinchonine may be separated from quinine by the insolubility of the former in cold alcohol. *Ether* dissolves all the alkaloids except morphine, cinchonine, strychnine, and brucine. *Chloroform* dissolves strychnine and most of those soluble in ether.

(β.) *Chemical.* The solutions of the alkaloids generally have an alkaline reaction. They act as bases, forming salts with acids. Kreatine is a neutral alkaloid, and not basic.

Action of Acids.—(1.) *Sulphuric acid,* when *concentrated,* slowly decomposes them, strychnine excepted; when *dilute,* it dissolves them and forms salts. With papaverine, it strikes a deep blue, thus distinguishing it from the other opium alkaloids. (2.) *Nitric acid* sometimes forms nitrates with the alkaloids, and sometimes colored compounds, as in the case of morphine, etc. (3.) *Hydrochloric acid,* forms with many of them additive compounds. With morphine, when heated in sealed tubes, it forms apomorphine. Apocodeine is formed by the action of the acid and zinc chloride on codeine. (4.) *Organic acids* combine with many of them, forming generally soluble salts. For example:—(α.) *Tannic acid* precipitates the salts of morphine, narcotine, codeine, cinchonine, quinine, strychnine, brucine, emetine, aconitine, atropine, delphinine, and veratrine. (β.) *Carbazotic acid* precipitates most of the alkaloids.

Action of Alkalies.—Alkalies decompose most of the alkaloids, when heated with them, with the evolution of ammonia.

Action of Haloids.—(1.) *Chlorine* usually decomposes alkaloids, forming hydrochloric acid, which combines with the base itself or with some substitution-compound produced by its action. Chlorine forms, (α.) with *strychnine,* a white precipitate; (β.) with *brucine, cinchonine,* and *morphine,* yellow precipitates, which change to red, and again to yellow; (γ.) with *narcotine,* a pale red precipitate, which becomes dark red, and then brown; (δ.) with *quinine* (on the addition of ammonia), an emerald green solution.

(2.) *Bromine* acts in most respects similarly to chlorine.

(3.) *Iodine* combines with most of the alkaloids to produce an insoluble yellow or brown compound of iodine and the alkaloid. This was first noticed by Pelletier in the case of strychnine, and was further investigated by Bouchardat. Herapath has pointed out that the crystalline compound of iodo-sulphate of quinine (Herapathite)

$C_{20}H_{24}N_2O_2I_2H_2SO_4(H_2O)_5$ exerts a powerful polarizing action on transmitted light.

Action of Metallic Salts.

(1.) *Platinic chloride*, forms crystalline compounds with the chlorides of the alkaloids.

(2.) *Mercuric chloride*, forms double salts with the chlorides.

(3.) *Auric chloride*, in some cases, produces a characteristic colored precipitate. Thus, with morphine, it produces a green; with strychnine, a yellow, etc.

(4.) *Ferric chloride*, forms a green compound with morphia.

Action of Nascent Oxygen.—Nascent oxygen decomposes many of the alkaloids, new compounds being formed. With strychnine, morphine etc., it gives a characteristic series of tints. (*See* page 11.)

The vegetable alkaloids are extensively used in medicine. As an antiperiodic, quinine is esteemed of great value. The ordinary sulphate of quinine is a basic sulphate, and has the formula $(C_{20}H_{24},N_2O_2)_2, H_2SO_4,8H_2O$. It is very slightly soluble in water. On adding a few drops of sulphuric acid to the basic sulphate suspended in water, a neutral sulphate is formed ($C_{20}H_{24}N_2O_2,H_2SO_4,7H_2O$), which is freely soluble. The tincture of quinine (B.P.) is an alcoholic solution of the basic sulphate. The tinctura quinæ ammoniata (B.P.) is an alcoholic solution of quinine precipitated by ammonia from a solution of a salt. The vinum quinæ is a mixed solution of the neutral sulphate, and citrate.

(A.) ALKALOIDS OF VEGETABLE ORIGIN.

Among the vegetable alkaloids, those which do not contain oxygen are liquid and volatile at ordinary temperatures, while those containing oxygen are solid, and for the most part non-volatile.

(1.) Non-oxygenated Alkaloids.

Name.	Formulæ.	Source.
Nicotine	$C_{10}H_{14}N_2$	Tobacco.
Conine	$C_8H_{15}N$	Hemlock.
Sparteine	$C_{15}H_{26}N_2$	Broom.

Nicotine, $C_{10}H_{14}N_2$.—This is the volatile alkaloid of the tobacco leaf. The leaf contains from 2 to 8 per cent. of nicotine combined principally with malic acid. Havanah tobacco contains only about 2 per cent., whilst Virginia contains about 7 per cent. of nicotine.

Preparation.—The powdered tobacco leaf is mixed with slaked lime, and put into a large flask on a water-bath. A current of steam is passed through the mixture, the flask being connected with a condensing apparatus. The liquid that distils over consists of water, nicotine, ammonia and other organic bases. This liquid is neutralized with sulphuric acid and concentrated. On the addition of ammonia to the concentrated solution, nicotine is liberated and can be separated by solution in ether. The ethereal solution on evaporation leaves nicotine, which may be purified by rectification.

Properties.—Nicotine, when pure, is a colorless oily liquid, boiling at 464° F. (240° C.). Its specific gravity at 60° F. is 1·027. It is soluble in water, the solution, even when dilute, having a burning taste. It is a powerful narcotic poison.

Conine, $C_8H_{15}N$.—Conine is the poisonous principle of the hemlock (*Conium maculatum*). It occurs in all parts of the plant, but is most abundant in the fruit.

Preparation.—It may be prepared from the seeds by distilling them with slaked lime, in a similar manner to that employed in the preparation of nicotine.

An artificial conine has been prepared by the distillation of *dibutyraldine,* a body formed by digesting normal butylic aldehyde with an alcoholic solution of ammonia.

Conine has been prepared synthetically by the reduction of *allylpyridine* ($C_5H_4N.C_3H_5$), a body formed by heating a mixture of paraldehyde and α-picoline at about 482°F. (250° C.). When this body is acted on with sodium it is reduced to α-propylpiperidine, which resembles conine in chemical composition, specific gravity, solubility and physiological action, but is optically inactive whilst conine is dextrorotary. This α-propylpiperidine has, however, been split up into two isomeric bodies, one of which is dextro-rotary and corresponds with conine, whilst the other is lævo-rotary.

Properties.—Conine is a colorless liquid, boiling at 413° F. (212° C.). Specific gravity, 0·89. It has a penetrating and peculiar odor, and a taste like that of nicotine. It is an active poison. It is only slightly soluble in water, but easily soluble in alcohol and in ether. It yields *butyric acid* on oxidation.

Sparteine, $C_{15}H_{26}N_2$.—This alkaloid was discovered by Dr. Stenhouse in the common broom (*spartium scoparium*).

Properties.—Sparteine is a colorless liquid, heavier than water. It boils at 591·8° F. (311° C.). It is slightly soluble in water, but freely soluble in alcohol and ether. It is a narcotic poison, but not so active as nicotine. On oxidation with permanganate of potass, sparteine yields oxalic acid and acetamide.

(2.) Oxygenated Alkaloids.

(*a.*) *Alkaloids of the Cinchona bark* (*and plants belonging to N.O. cinchonaceæ*).

Name.	Formulæ.	Name.	Formulæ.
Cinchonine	$C_{20}H_{24}N_2O$.	Quinine	$C_{20}H_{24}N_2O_2$
Cinchonidine	Isomeric with above.	Quinidine	Isomeric with Quinine.
Cinchonicine		Quinicine	
Aricine (*Cusso bark*)	$C_{23}H_{26}N_2O_4$	Quinoidine	
Emetine (*Ipecacuanha*)	$C_{30}H_{44}N_2O_8$	Homo-quinine	

Cinchona bark contains, besides the above alkaloids, quinic, quinovic and quinotannic acids, coloring matters, and a green fatty matter. The value of the bark to the manufacturer depends on its percentage of quinine. This varies in the different barks, in grey barks from 0·3 per cent., in red barks from 0·9 per cent., and in yellow barks from 2 per cent.

Extraction of the Alkaloids from the Bark.

The powdered bark is boiled with ten times its weight of water acidulated with 10 per cent. of sulphuric acid. The decoction is filtered, and a slight excess of milk of lime added. The precipitate is collected, dried, and heated over a water bath with strong alcohol. The cinchonine is deposited from the solution on cooling, whilst the quinine remains in the mother-liquor.

Cinchonine, $C_{20}H_{24}N_2O$.

Properties.—Forms colorless, anhydrous crystals, fusing at 329° F. (165° C.). It is insoluble in cold water, and much less soluble than quinine in alcohol (1 in 35). It is insoluble in ether, and only slightly soluble in chloroform. The alcoholic solution of cinchonine turns the plane of polarization to the right.

Quinine, $C_{20}H_{24}N_2O_2$.—The extraction of quinine from the bark by means of lime and alcohol has already been described, also its separation from cinchonine. The quinine can be extracted from the lime precipitate by means of hot petroleum, which dissolves all the quinine and but very little of the cinchonine. On shaking the petroleum extract with dilute acid, the petroleum gives up the quinine to the acid solution.

Properties.—Quinine is a white powder, fusing at 248° F. (120° C.). It is without odor and has a very bitter taste. It is used in medicine for its tonic and antifebrile properties. Its alcoholic solution turns the plane of polarization to the *left*. It is less soluble in water than cinchonine (1 in 360 of cold water). It is readily soluble in alcohol, in ether, and in chloroform. The chief salts used in medicine are the neutral sulphate $[2(2C_{20}H_{24}N_2O_2.H_2SO_4).15H_2O]$, the acid sulphate $(C_{20}H_{24}N_2O_2.H_2SO_4.15H_2O)$, and the citrate $(2C_{20}H_{24}N_2O_2.C_6H_8O_7)$.

If an alcoholic solution of iodine be added to a solution of acid sulphate of quinine in acetic acid, a sulphate of iodoquinine $(2C_{20}H_{24}N_2O_2.3H_2SO_4.I_6)$ is formed. This salt crystallizes in flat plates of an emerald-green color, possessing all the optical properties of tourmaline.

Quinidine.—It is prepared from commercial quinoidine, which yields about 50 to 60 per cent. of quinidine. It is soluble in ether and in alcohol, and but very slightly soluble in water (1 in 1500). Its solution in alcohol turns the plane of polarization to the right.

Quinoidine.—This is a brown resinous mass, obtained as a bye product in the extraction of quinine and cinchonine from the bark. It is insoluble in water, but soluble in alcohol and in ether.

Aricine, $C_{23}H_{26}N_2O_4$.—Aricine is an alkaloid specially found in cusso or arica bark. It forms white prismatic crystals, very sparingly soluble in water. It dissolves in strong nitric acid with decomposition, forming a deep green solution.

(*b.*) *The Opium Alkaloids.*

Opium.—Opium is the dried juice obtained from the unripe capsules of the white poppy (*Papaver somniferum*). It is a brown substance having a bitter acrid taste and peculiar odor. It contains several alkaloids, combined chiefly with meconic acid :—

Name.	Formulæ.
Morphine	$C_{17}H_{19}NO_3$
Narcotine	$C_{22}H_{23}NO_7$
Codeine	$C_{18}H_{21}NO_3$
Thebaine	$C_{19}H_{31}NO_3$
Narceine	$C_{23}H_{29}NO_9$
Papaverine	$C_{20}H_{21}NO_4$

Morphine, $C_{17}H_{19}NO_3$.—This is the most important alkaloid of the opium bases.

Preparation.—Opium is exhausted with water at 100·4° F. (38° C.), the solution decanted and evaporated with calcium carbonate, which neutralises the free acid. When the liquid is sufficiently concentrated, chloride of calcium is added, whereby meconate of lime is precipitated, together with a considerable quantity of coloring matter. The opium bases remain in solution as hydrochlorates, and on further evaporation of the solution crystallise out. The hydrochlorates are dissolved in water and excess of ammonia added, which precipitates the morphine, the codeine remaining in solution.

Properties.—Morphine is very slightly soluble in cold water or in cold alcohol. It is insoluble in ether. It has no odor, a slightly alkaline reaction, and a bitter taste. The hydrochlorate and acetate are used in medicine as sedatives.

Codeine.—$C_{18}H_{21}NO_3$.—This alkaloid is obtained from the mother-liquor after the morphine has been removed by ammonia.

Properties.—Codeine is more soluble in water than morphine (100 parts water dissolves 1·26 parts codeine). It dissolves freely in alcohol and in ether, and is also soluble in ammonia. Its physiological action resembles that of morphine.

(*c.*) *The Strychnia Alkaloids.*

Strychnine, together with brucine exists in nux-vomica, S. Ignatius Bean, in the wood of *Strychnos Colubrina* and other varieties of *Strychnos.*

Preparation.—From nux-vomica. The softened and pulverised nux-vomica is digested with alcohol (Sp. Gr. 0·856) acidulated with sulphuric acid. Lime is added to the solution thus obtained to remove the acid and precipitate some of the coloring matter. The liquid is decanted and distilled, the residue being saturated with dilute sulphuric acid, filtered, and the filtrate concentrated. Ammonia is then added to the concentrated solution, and the precipitate produced collected and dried. The dried precipitate is then digested with weak alcohol (Sp. Gr. 0·942) to dissolve out the brucine. The residue is then dissolved in strong hot alcohol and crystallised.

Properties.—Crystallises in white prisms, which may be fused without decomposition. It has no odor, an intensely bitter taste, and is very poisonous. Strychnine is slightly soluble in water (1 part in 6,600), and very soluble in alcohol and in chloroform. It is also soluble in strong sulphuric acid without decomposition.

The chief salts of strychnia are the hydrochloride ($C_{21}H_{22}N_2O_2.HCl$), and the sulphate ($2C_{21}H_{22}N_2O_2.H_2SO_4$).

Brucine, $C_{23}H_{26}N_2O_4$.—The preparation of this alkaloid from nux-vomica has already been described. It also occurs, however, unaccompanied by strychnine, in false angostura bark. Brucine is poisonous, the symptoms produced being similar to those of strychnine but much less energetic. It dissolves in nitric acid with decomposition, forming a red solution. It turns the plane of polarization to the left.

(*d.*) *Alkaloids from various Sources.*

Aconitine, $C_{30}H_{47}NO_7$.—The alkaloid of the Aconites. It is sparingly soluble in water (1 in 150 at 15° C.), but soluble in alcohol and in ether. It is intensely poisonous.

Caffeine or Theine, $C_{16}H_{10}N_4O_4$.—This alkaloid occurs in the berries and leaves of the coffee plant, and in the leaves and twigs of the tea plant.

Preparation.—Ground coffee or tea is mixed with slaked lime and the mixture exhausted with alcohol. The clear alcoholic solution is then distilled and the residue dissolved in boiling water. The caffeine or theine crystallises out on cooling.

These alkaloids may also be prepared by sublimation. For this purpose the tea is placed in a sublimation apparatus and heated, care being taken that the heat employed is not sufficient to decompose the alkaloid. The alkaloid sublimes and may be purified by crystallization from water.

Properties.—Caffeine crystallizes from water in white, silky needles. Melts at 352·4° F. (178° C.) and sublimes at 365° F. (185° C.). It is only slightly soluble in cold water or in alcohol, but it dissolves freely in hot water.

Theobromine, $C_7H_8N_4O_2$.—An alkaloid existing in the cacao-bean, from which it may be extracted by boiling water, and purified by sublimation. It forms white silky crystals, which sublime about 354° F. (290° C.) without change. It has a bitter taste, and is very slightly soluble in alcohol and in ether.

Cocaine, $C_{32}H_{19}NO_8$.—Cocaine is prepared from the leaves of coca (*erythroxylon coca*) by solution in alcohol, acidulated with sulphuric acid. The alkaloid may be precipitated from this solution with lime, etc.

Properties.—Cocaine crystallizes in small colorless prisms. It has a bitter taste, and produces insensibility on the part of the tongue to which it is applied. It is soluble in 705 parts of cold water, but is more soluble in alcohol and ether. The hydrochlorate of cocaine is easily soluble in water, and this aqueous solution is used in medicine as a local anæsthetic.

Veratrine, $C_{32}H_{52}N_2O_8$.—This alkaloid occurs in sabadilla seeds, in white hellebore (*veratrum album*) and in other species of veratrum.

Properties.—It is insoluble in water, but very soluble in alcohol and in ether. It has no odor, but if small quantities get into the nose, it occasions violent sneezing. It is very poisonous in small doses, it possesses an antifebrile action.

Piperine, $C_{17}H_{19}NO_3$.—This alkaloid exists in long and black pepper (*piper longum* and *piper nigrum*), and may be extracted, therefrom, by strong alcohol.

Properties.—Piperine crystallises in colorless prisms, which melt at 212° F. (100° C.), forming a yellow oil. The crystals are insoluble in cold, but slightly soluble in hot water. The alcoholic solution has a hot taste like that of pepper.

Atropine $C_{17}H_{23}NO_3$.—Atropine occurs in all parts of the deadly nightshade (*atropa belladonna*), also in the seeds of the thornapple (*datura stramonium*), etc. It crystallizes in silky needles, which are slightly soluble in water, but easily soluble in alcohol. It is very poisonous.

Berberine, $C_{20}H_{17}NO_4$. Berberine is found in the root of the barberry (*berberis vulgaris*), and also in colombo-root (*cocculus palmatus*).

Physostigmine, $C_{30}H_{21}N_3O_4$.—Physostigmine is the poisonous alkaloid of the calabar bean (*physostigma venenosum*). It is easily extracted from the bean by boiling alcohol, which on evaporation leaves an amorphous mass, slightly soluble in water, but freely soluble in alcohol and in ether.

Hyoscyamine, $C_{15}H_{23}NO_3$.—An alkaloid contained in henbane (*hyoscyamus niger*). It crystallises from alcohol in silky needles, but is generally obtained as a sticky mass. When moist it has the odor of tobacco. It is soluble in water, in alcohol, and in ether.

Asparagine, $C_4H_8N_2O_3$.—This alkaloid occurs in the young shoots of the asparagus. It forms hard brittle crystals, soluble in water, but insoluble in alcohol and in ether.

(B.) ALKALOIDS OF ANIMAL ORIGIN.

Name.	Formulæ.	Source.	Properties, etc.
Xanthine	$C_5H_4N_4O_2$	Urinary calculi, guanine, urine, all parts of body. Formed by the action of nitrous acid on guanine.	A white amorphous body, soluble in acids, forming salts; slightly soluble in boiling water; soluble in alkaline solutions. Dissolves in HNO_3, without the evolution of any gas, leaving a yellow residue which turns red with ammonia. The hydrochloride is insoluble in water.
Hypoxanthine (Sarcine	$C_5H_4N_4O$	Flesh of vertebrata, also in blood, liver, etc.	White crystals, soluble in boiling (but not in cold) water, and in dilute acids and alkalies. The hydrochloride is soluble in water.
Guanine	$C_5N_5H_5O$	Guano, excrement of spiders; pancreatic juice.	Colorless crystals; insoluble in water, alcohol, ether, and ammonia; soluble in acids and in a potash solution. Forms salts. By the action of $KClO_3$ and HCl it forms *parabanate* ($C_3H_2N_2O_3$) and *guanadine*, (CH_5N_3).
Kreatine	$C_4H_9N_3O_2.2aq$	Flesh, urine, brain	Colorless crystals; soluble in boiling water; sparingly soluble in cold water (1 in 74); insoluble in alcohol or ether. Solution bitter. Kreatine is a neutral body, combining neither with acids nor alkalies.
Kreatinine	$C_4H_7N_3O$	Ditto.	Prepared by the action of strong acids on kreatine. It forms crystals, soluble in water (1 in 11 at 60° F.), the solution being very alkaline. It forms salts with acids. It evolves *methylia* when heated with soda lime. By boiling with an alkali it forms kreatine.
Sarcosine	$C_3N_7HO_2$	Ditto.	Prepared by boiling kreatine with baryta water.

	Name.	Formulæ.	Source.	Properties.
	Urea	CN_2H_4O	Urine	(*See* page 826.)
Ptomaines.	Tetanine	$C_5H_{11}N$	Beef extract	Forms a crystalline hydrochloride soluble in water and alcohol. When injected hypodermically produces tetanus.
	Xanthocreatinine ..	$C_5H_{10}N_4O$	Muscle	
	Crusocreatinine ..	$C_5H_8N_4O$		
	Amphicreatinine ..	$C_9H_{19}N_7O_4$		
	Pseudoxanthine ..	$C_4H_5N_5O$		

Constitution of the Alkaloids.

(1.) *Berzelius* regarded the alkaloids as conjugate bodies of some neutral substance with ammonia (to which latter compound he supposed they owed their alkalinity), founding this theory on the universal presence in these bodies of hydrogen and nitrogen. To this, objection was made that it was impossible to detect the presence of ammonia in them.

(2.) *Liebig* regarded them as ammonias, where one atom of hydrogen was replaced by a compound radical ; in other words, as compounds of amidogen (NH_2) with a compound radical capable of acting as a hydrogen atom, and not destructive to the original alkalinity. Thus in *aniline*, $NH_2(C_6H_5)$, one hydrogen was regarded as having been replaced by one of phenyl (C_6H_5). This view of the composition of aniline was confirmed by the circumstance that aniline was obtained by the action of heat on ammonic phenate. Thus—

$$NH_4.C_6H_5O \text{ (\textit{ammonic phenate})} = NH_2(C_6H_5) \text{ \textit{aniline}} + H_2O.$$

Hence an *amide* was regarded as a body derived from an ammoniacal salt by the loss of a water molecule.

(3.) Further investigation has shown that in organic bases—

(*a.*) One, two or three atoms of the hydrogen of ammonia may have been displaced by one, two or three molecules of a univalent compound radical or their equivalent, and that—

(*β.*) The nitrogen of the ammonia may also be displaced by certain elements, such as phosphorus, arsenic, antimony, etc.

It is important for us to consider here the method of investigation pursued in these inquiries:—

(1.) If ammonia and ethylic iodide (C_2H_5I) be heated in a sealed tube, the apparently conjugate body NH_3,C_2H_5I is formed. When this compound, however, is distilled with potassic hydrate, it yields (not ammonia, but) *potassic iodide* and *ethylamine*, this latter body being ammonia where one of hydrogen has been displaced by one of the alcohol or hydrocarbon radical ethyl (C_2H_5). Thus—

$$NH_3.C_2H_5I + KHO = NH_2(C_2H_5) + KI + H_2O.$$

+ Potassic hydrate = Ethyl-amine + Potassic iodide + Water.

Nevertheless, ethylamine is a colorless and alkaline liquid, forming salts with acids, boiling at 65·6° F. (18·7° C.), and smelling of ammonia.

(2.) If a mixture of ethylamine and ethylic iodide be heated as before in a sealed tube, the compound $NH_2(C_2H_5)C_2H_5I$ will be formed. This, on being distilled with potassic hydrate, furnishes *potassic iodide* and *diethylamine*, this latter compound being an ammonia where two atoms of hydrogen are replaced by two molecules of the alcohol radical ethyl (C_2H_5). Thus—

$$NH_2.C_2H_5.C_2H_5I + KHO = NH(C_2H_5)_2 + KI + H_2O.$$

+ Potassic hydrate = Diethylamine + Potassic iodide + Water.

Nevertheless, diethylamine is a colorless and alkaline liquid, boiling at 134·6° F. (57·0° C.), and behaving chemically as ammonia.

(3.) Similarly, *diethylamine*, $NH(C_2H_5)_2$, may be converted into *triethylamine*, $N(C_2H_5)_3$, which is also a colorless and alkaline liquid.

(4.) If triethylamine $N(C_2H_5)_3$ be similarly heated with ethylic iodide, the conjugate compound $N(C_2H_5)_3.C_2H_5I$ is formed.

(5.) But in the same manner that we regard the hydriodate of ammonia as an iodide of the hypothetical metal ammonium (NH_4), thus—

$(NH_3)HI$ (*hydriodate of ammonia*) $= (NH_4)I$ (*iodide of ammonium*),

so we may regard the compound $(N(C_2H_5)_3C_2H_5I)$ as the *iodide of tetrethylammonium* $(N(C_2H_5)_4I)$, or, in other words, as a compound where the four atoms of the hydrogen of the metal ammonium have been replaced by four of ethyl.

(6.) On heating this body $(N(C_2H_5)_4I)$ with potassic hydrate, it is *not* decomposed. When its solution, however, is treated with argentic oxide, argentic iodide is precipitated, and a solution of tetrethylammonic hydrate is formed. Thus—

$$2[N(C_2H_5)_4I] + Ag_2O + H_2O = 2[N(C_2H_5)_4HO] + 2AgI.$$

Iodide of tetrethylammonium + Argentic oxide + Water = Tetrethylammonic hydrate + Argentic iodide.

This hydrate, which may be obtained in a crystalline state by evaporation "in vacuo," is an alkaline, caustic, deliquescent body, freely absorbing carbonic anhydride from the air, expelling ammonia from its salts, forming salts with acids, forming a soap with fat, etc. In other words, we have points of close relationship, chemically, between tetrethylammonic hydrate and potassic or ammonic hydrates. Thus—

KHO;	$(NH_4)HO$;	$(N(C_2H_5)_4)HO$.
Potassic hydrate;	Ammonic hydrate;	Tetrethylammonic hydrate.

(7.) In like manner experiments might be conducted on ammonia with the iodides of other alcohol radicals, as of methyl (whereby methylamine would be produced); or of amyl (forming amylamine, etc.). Or, again, one hydrogen may be replaced by one radical, and one by another. Thus, if we act on aniline or phenylamine ($NH_2C_6H_5$), in succession first, with iodide of methyl (CH_3I), and distil with potash, then with iodide of ethyl $(C_2H_5)I$, and distil with potash, and lastly, with iodide of amyl ($C_5H_{11}I$), and distil, we obtain a compound formed on the ammonium type, where each hydrogen atom is replaced by a different compound alcohol radical. Thus we obtain—

$$N(C_6H_5)\ (CH_3)\ (C_2H_5)\ (C_5H_{11})HO.$$

Hydrate of phenyl-methyl-ethyl-amyl ammonium.

(8.) From these experiments we learn—

(α.) That by heating ammonia with ethylic iodide, and distilling the product with potassic hydrate, we obtain products where the hydrogen is replaced successively by C_2H_5. Thus we obtain—

First;	Ethylamine,	$NH_2(C_2H_5)$	when	H_1	is replaced by	C_2H_5.
Secondly;	Diethylamine,	$NH(C_2H_5)_2$	„	H_2	„	$(C_2H_5)_2$
Thirdly;	Triethylamine,	$N(C_2H_5)_3$	„	H_3	„	$(C_2H_5)_3$.

(β.) That by the further action of ethylic iodide on triethylamine, a compound is formed containing another ethyl molecule, *viz.*, $N(C_2H_5)_4I$, corresponding to the salt NH_4I.

(γ.) That this product, unlike the previous compounds, is not decomposed by the action of potassic hydrate, but may be made to yield a caustic alkaline liquid $N(C_2H_5)_4(HO)$, closely related in chemical reactions and properties to $NH_4(HO)$.

9. Adopting a similar method of investigation in examining the constitution of the alkaloids to that above described in the case of ammonia, we ask this question—

How many atoms of hydrogen in the alkaloid can be replaced by an alcohol radical (such as ethyl), by the action upon the alkaloid of iodide of ethyl?

For example:—

Conine has the formula $C_8H_{15}N$. We act upon it with ethylic iodide, and distil the product with potassic hydrate, when we obtain—

$$C_8H_{14}(C_2H_5)N.$$

Thus we learn for certain that one atom of the hydrogen of the conine can be replaced by C_2H_5.

We again act on the new body formed ($C_8H_{14}(C_2H_5)N$) with ethylic iodide, and we obtain the product $C_8H_{14}(C_2H_5)_2NI$, where, although the body has taken up a new molecule of C_2H_5, nevertheless another hydrogen atom has not been displaced. Further, it will be found that the new product is not decomposed when treated with potassic hydrate, and may be converted by argentic oxide into a soluble base corresponding to $(NH_4)HO$.

Hence our experiments prove that only one hydrogen atom of the alkaloid conine $(C_8H_{15}N)$ can be replaced by ethyl, and that therefore the group (C_8H_{14}), supposing conine to be an ammonia, must play the part of two hydrogen atoms. Therefore the formula

$$N\left\{\begin{matrix}(C_8H_{14})'' \\ H\end{matrix}\right. \text{ or } NH(C_8H_{14})''$$

may be taken to represent the constitution of conine as an ammonia.

10. Again, *morphine* has the formula $C_{17}H_{19}NO_3$. Heated with ethylic iodide, it forms $C_{17}H_{19}(C_2H_5)NO_3I$, *i.e.*, it refuses to part with any of its hydrogen under the action of ethylic iodide. Hence the formula $N(C_{17}H_{19}O_3)'''$ represents the constitution of morphine, exhibiting it as an ammonia where the group $C_{17}H_{19}O_3$ plays the part of three atoms of hydrogen.

11. Some alkaloids containing two atoms of nitrogen are regarded as being built up on the double ammonia type (N_2H_6); others, containing three of nitrogen, on the treble ammonia type (N_3H_9), etc. Thus :—

$$N_2(C_{20}H_{24}O_2)^{vi}=\text{Quinine}\ ;\ \ N_2(C_{21}H_{22}O_2)^{vi}=\text{Strychnine.}$$

REACTIONS OF THE ALKALOIDS.

Quinine.—1. Crystals; tufts of needles. Solutions of quinine salts are fluorescent.

2. *Solubility.* Soluble in alcohol, ether, etc.; slightly soluble in water.

3. *Heat.* (1.) Entirely dissipated and decomposed when heated on platinum foil. (2.) Give a violet-red sublimate, with quinoline odor, when heated in a test-tube.

4. *Sulphuric acid* dissolves it. The color produced is a faint yellow. (Salicine gives a red.)

Nitric acid dissolves it. No color produced, but the solution turns yellow when heated.

Chlorine water and ammonia; a bright green solution.

Chlorine water, potassic ferrocyanide, and ammonia; a deep evanescent red solution.

5. Turns the plane of polarization to the *left.*

Cinchonine.—1. Crystals; four-sided prisms. Solutions of cinchonine salts are not fluorescent.

2. *Solubility.* Soluble in alcohol; very slightly soluble in water; insoluble in ether.

3. *Heat.* Similar to quinine.

4. *Chlorine water and ammonia;* a yellowish white precipitate.

5. Turns the plane of polarization to the *right.*

Morphine.—1. Crystals; four-sided prisms. Taste, bitter.

2. *Solubility.* Soluble in water and alcohol; insoluble in ether.

3. *Heat.* Melts, inflames like resin, leaving a little charcoal, which soon burns away.

4. *Nitric acid* turns it red; color destroyed by $SnCl_2$ and $(NH_4)_2S$. (*See* Brucine.)

Sulphuric acid dissolves it; solution colorless.

Ferric chloride (Fe_2Cl_6 neutral) colors it blue.

Narcotine.—1. Crystals; rhombic prisms.

2. *Solubility.* Insoluble in water; soluble in alcohol and ether.

3. *Heat.* Fuses and is finally dissipated.

4. *Sulphuric acid.* A red color when heated.

Chlorine water and ammonia; a yellowish-red liquid.

Atropine.—1. Crystals; silky needles.

2. *Solubility.* Slightly soluble in water and ether; soluble in alcohol and chloroform.

3. *Heat.* Fuses at 194° F., decomposes and partially sublimes.

4. *Auric chloride;* a yellow precipitate.

Aconitine.—1. Crystals not well marked. When a minute particle is placed on the tongue, it produces tingling and numbness.

2. *Solubility.* Slightly soluble in cold water, soluble in alcohol and ether.

3. *Phosphoric acid;* a violet tint.

Sulphuric acid turns it yellow, changing to a dirty violet.

Strychnine.—1. Crystals; octahedra. Taste intensely bitter.

2. *Solubility.* Soluble in chloroform and methylic alcohol; slightly soluble in water and dilute alcohol; insoluble in absolute alcohol or ether.

3. *Heat.* Slightly volatile.

4. *Sulphuric acid* dissolves it without change of color; on adding MnO_2 or PbO_2, etc., to the acid solution, a play of color from purple violet to red is obtained.

5. The physiological test on a frog is infinitely the most delicate.

Brucine.—1. Crystals; needles arranged in stars.

2. *Solubility.* Soluble in water and alcohol; insoluble in ether.

3. *Nitric acid.* A bright red; becoming yellow by heat; violet by $SnCl_2$ or $(NH_4)_2S$. (*See* Morphine.)

4. *Chlorine water.* A red solution, becoming yellow with ammonia.

Caffeine.—1. Crystals; silky needles. Taste very bitter.

2. *Solubility.* Soluble in water, alcohol and ether.

3. *Heat.* Melts and sublimes.

4. *Nitric acid.* Solution red when evaporated to dryness; turns purple on adding ammonia.

Urea.—1. Crystals ; four-sided prisms permanent in air.

2. *Solubility.* Soluble in water and alcohol ; insoluble in ether

3. *Heat.* Evolves NH_3 ; partially sublimes.

4. *Nitric acid.* Forms crystals of nitrate of urea.

Potassic hydrate and heat ; evolves ammonia.

Oxalic acid. Deposits tabular crystals.

CHAPTER XXIX.

COLORING MATTERS.

Natural History — General Preparation and Properties — Yellows — Reds — Blues — Browns—Blacks.

SUPPLEMENTARY CHAPTER: Dyeing and Calico Printing.

Natural History.—A few coloring bodies are found (1) in the *animal* kingdom, *e.g.*, cochineal and sepia, but they occur almost entirely (2) in the *vegetable* kingdom.

Preparation.—(1.) By solution in water, spirit, ether, or oils.

(2.) By fermentation (*e.g.*, indigo, madder, archil, and litmus).

Preparation of Indigo.—The leaves of plants of the species indigofera, are placed in water and allowed to ferment. A yellow soluble substance is first formed, which in time turns blue, and becomes insoluble. This constitutes, when dried, the indigo of commerce. The change of color is due to the oxidation of a body existing in the plant, called *indican.*

Preparation of Madder.—Madder is prepared by a similar method of fermentation, whereby a yellow substance present in the plant, called *rubian* ($C_{28}H_{34}O_{15}$), becomes converted into alizarine ($C_{14}H_8O_4$).

Preparation of Archil and Cudbear.—The plants are first digested with lime and water, and the clear filtered solution neutralised with hydrochloric acid. The white precipitate thus produced, consisting of one or more acids, such as erythric, evernic, and lecanoric acids, is dissolved in hot alcohol. This solution is then boiled with lime, by which means the acids are decomposed. The clear solution from which the excess of base has been removed yields, on evaporation and extraction with boiling alcohol, the colorless body called *orcine* ($C_7H_8O_2$), which by the action of air and ammonia forms the red coloring matter *orceine* ($C_7H_7NO_3$).

In practice the *archil* and the *cudbear* are mixed with lime and urine (the latter to furnish ammonia), and the mixture exposed to the air for some weeks. In the case of *litmus,* ammonic and potassic carbonates are used instead of lime and urine. The red color produced in the case of litmus is *azolitmine* ($C_7H_{10}NO_5$), which differs from orceine in its insolubility in alcohol.

(3.) By artificial processes :—*e.g.*, indigo-blue, which is prepared from aceto-phenone, alizarin from anthracene, etc.

Properties.—General.—The organic coloring matters are solid bodies. Some of them are crystalline, such as alizarin, moritannic acid, hæmatoxylin, etc.

Their colors are bright; they have but little taste or odor.

Heat decomposes most of them. A few are volatile (*e.g.*, indigo, alizarine).

Light bleaches most of them, especially if the coloring matter be moistened with water.

They are mostly soluble in water, but are insoluble in alcohol or in ether.

Strong acids generally decompose them, sulphuric acid charring, and nitric acid oxidizing them. Weak acids change the blues to reds. Cyanine, for example, is the blue coloring matter of certain flowers, and the flower is *blue* if its juice be neutral, but *red* if it be acid.

They are all bleached by chlorine, by sulphurous acid, by reducing agents, and generally also by the action of nascent oxygen.

Alkalies change the reds to greens or blues, and the yellows to browns.

The metallic oxides combine with many of them to form permanent compounds (*e.g.*, the lakes). Thus alumina, ferric oxide, and stannic oxide are used as mordants. Charcoal generally both absorbs and destroys the colors.

I. The Yellows.

1. *Annatto* (seeds of Bixa Orellana).—The coloring matter "bixine" is soluble in alkalies.

2. *Chrysammic Acid.*—Prepared by the action of nitric acid on aloes.

3. *Gamboge* (Hebradendron Gambogioides).—A gum resin, the coloring matter being soluble in water.

4. *Hæmatoxylin* (Logwood; Hæmatoxylon Campechianum).—It forms the red *hæmatein* ($C_{16}H_{12}O_6$) in contact with oxygen and alkalies, and a black by the action of potassic chromate.

5. *Luteoline or Weld* (Reseda Luteola).—Soluble in water.

6. *Morindin* (Morinda Citrifolia) (*Soranjee*).

7. *Moritannic Acid* (Morus Tinctoria or Fustic).—Soluble in water.

8. *Oxypicric Acid.*—Prepared by the action of nitric acid on assafœtida.

9. *Phylloxanthin.*—Phylloxanthin is precipitated by boiling chlorophyll in an alcoholic solution of potash, and adding hydrochloric acid to the solution.

10. *Picric Acid* is a derivative of phenol, and also a product of the action of nitric acid on indigo.

11. *Purree or Indian Yellow* (origin ?).—A compound of magnesia and purreic or euxanthic acid.

12. *Quercitrin* (Quercus Tinctoria).

13. *Rubian* (*See* Madder).

14. *Saffron* (Yellow Anthers of Crocus Sativus).—A glucoside.

15. *Turmeric* (Curcuma Longa).—The coloring matter *curcumine* is soluble in alcohol, but insoluble in water.

16. *Xanthin and Xantheine.*—The yellow coloring matter of flowers and of yellow leaves.

II. The Reds.

1. *Alizarin* (*See* Madder).

2. *Braziline.*—$C_{22}H_{20}O_7$, obtained from Brazil wood.

3. *Carmine; Cochineal;* (from insects of cocus tribe).—Cochineal is extracted by water and alcohol. The coloring body is *carminic acid* ($C_{14}H_{14}O_8$), which combines with alumina to form lakes.

4. *Draconine* (Dracœna Draco).

5. *Hœmatein* (*See* Hæmatoxylin).

6. *Madder Red* (Rubia Tinctorum).—By the fermentation of the yellow coloring glucoside *rubian* or ruberythric acid ($C_{20}H_{22}O_{11}$), whereby *alizarin* is formed ($C_{14}H_8O_4$).

7. *Orceine* ($C_7H_8O_2$).

8. *Safflower* (petals of Carthamus Tinctorius).—The coloring matter *carthamine* ($C_{14}H_{16}O_7$) is soluble in alkalies and is reprecipitated by acids.

9. *Santaline* (Pterocarpus Santalinus).

III. The Blues.

1. *Cyanine.*—This constitutes the blue coloring matter of flowers and also the coloring matter of grapes.

2. *Indigo* (various species of indigofera) (*See* General Preparation, page 783).—By the action of deoxidizing agents and an alkali, indigo becomes soluble and colorless (indigo white), changing to blue on exposure to air. Traces of indigo have been found in the urine.

Blue indigo ... ... $C_{16}H_{10}N_2O_2$.
White indigo ... ... $C_{16}H_{12}N_2O_2$.

By oxidation, indigo forms *isatin* ($C_{16}H_{10}N_2O_4$), which, by the action of chlorine upon it, forms *chlorisatin* ($C_{16}H_8Cl_2N_2O_4$).

3. *Litmus, Archil* and *Cudbear* (from various lichens, as Roccella Tinctoria (litmus), Lecanora Tartarea (cudbear)). These colors are developed by fermentation, whereby *orceine* ($C_7H_7NO_3$) is formed. (*See* General Preparation.)

4. *Phyllocyanine.*—From chlorophyll. This coloring matter remains in solution after the phylloxanthin has been precipitated.

IV. The Greens.

1. *Chlorophyll.*—A resinoid body present in plants. It is soluble in ether, and consists of phylloxanthin (a yellow) and phyllocyanine (a blue).

V. Brown.

Sepia, from the cuttle fish.

VI. Black.

See Hæmatoxylin.
Pigmentum Nigrum.

SUPPLEMENTARY CHAPTER.

DYEING AND CALICO-PRINTING.

Dyeing.—To obtain uniformity of color it is necessary that the coloring matter should be applied to the fabric in solution; but it is also essential, in order that the color should not be discharged when the fabric is washed, that it should be rendered insoluble in the fibre.

Sometimes the fibre itself forms an insoluble compound with the coloring matter. Thus, animal fabrics (such as silk and wool) combine with coloring matters; but if this does not happen, as in the case of cotton, other systems have to be adopted, such as the following:—(*α.*) The fibre is sometimes impregnated with a material called a mordant, such mordant being capable of forming an insoluble compound with the coloring matter (*e.g.*, alumina and cochineal). (*β.*) In the case of a color formed by the admixture of solutions, the fabric is first saturated with one solution and then dipped into the second, so that the insoluble coloring matter may be formed in the fabric itself. (Thus, a blue dye is formed from ferric chloride and potassium ferrocyanide.)

The *red dyes* used are madder and brazil wood, alum and bitartrate of potash being the mordants employed. Lac or cochineal are used for dyeing wool, stannic chloride and bitartrate of potash being used as mordants. The aniline colors are also employed, albumen being required as a mordant in dyeing cotton, no mordant being necessary for wool or silk.

The *blues* used in dyeing are usually *indigo,* the aniline blues, and Prussian blue, the latter being formed by the admixture of solutions of ferric chloride and potassic ferrocyanide.

The *yellows* employed are weld, quercitron, fustic, annatto (aluminous mordants being used for each of these dyes), lead chromate (formed by the admixture of acetate of lead and potassic chromate), and carbazotic acid.

Browns and blacks are formed by a mixture of tannin and a salt of iron, different shades depending on the relative proportions of each, or by the admixture of indigo, etc.

Calico Printing.—This consists in the production of a pattern on the fabric. This is effected in different ways: (1.) By printing the pattern on the fabric with the mordant mixed with gum. By the action of water containing cow-dung or some dung substitute (*dunging*) any excess of mordant may be removed. The fabric is then dipped in the dye-bath; any color taken up, except that on the mordanted pattern, can be washed out with water. (2.) Sometimes a *resist* is used, that is, a substance like citric or tartaric acid, which prevents the fabric taking the color on those parts to which the resist has been applied. (3.) Sometimes a *discharge* is used. The color from a uniformly printed fabric dyed with indigo, madder, etc., may be removed wherever desired by the application of an acid mixed with gum, and afterwards passing the fabric through a solution of chloride of lime. By this means the color will be discharged wherever the acid has been placed. Different colors may also be produced at the same time, by combining the acid with different reagents.

CHAPTER XXX.

VEGETABLE CHEMISTRY.

Tissues of Vegetable—Cellulin—Vegetable Parchment—Gun Cotton—Woody and Corky Tissue—The Life of a Plant.

THE organised structures of plants are made up of three kinds of material :—

(1.) *Cellulin* (*lignin*) $(C_6H_{10}O_5)_n$. This constitutes the growing part of the plant, such as the cambium layer, etc.

(2.) *Woody matter* (*sclerogen*), such as the duramen or alburnum.

(3.) *Corky matter.* Of this material the outer layer of the plant is composed.

In cellulin, the hydrogen and oxygen are present in the proportion to form water, but in woody tissue and in corky matter the proportions are different.

I. Cellulin (*lignin ; cellulose*) $(C_6H_{10}O_5)_n$. This constitutes the growing and active part of the plant. It forms the basis of vegetable cells and of the true cell-wall. In its purest form it is met with in the extremities of the roots and buds, in the pith or medulla, in the medullary rays, in the cambium or under layer of the bark, and in certain hairs or filaments about the seeds, such as cotton, etc. Fungi, and the substance called vegetable ivory, are said to consist of nearly pure cellulin.

Preparation.—The adhesion of the encrusting woody tissue of the plant to the cellulin is so great, that it is scarcely possible to prepare it in a state of absolute purity. By the consecutive action of various solvents, such as water, alcohol, ether, dilute alkalies, and acids, etc., a condition of *comparative* purity may be effected.

Properties.—(*a.*) *Physical.* A tasteless, colorless, and innutritious substance. Specific gravity, 1·9. Its appearance varies : thus it is *spongy* in the shoots of germinating seeds ; *porous* and *elastic* in the pith of the rush and elder ; *flexible* and *tenacious* in the fibres of the hemp and flax ; *compact* in the branches of growing trees ; *hard* and *dense* in the shells of the filbert, etc. Cellulin possesses the power of depolarizing a ray of polarized light.

(*β.*) *Chemical.* Cellulin is insoluble in hot or in cold water, in alcohol, in ether, or in oils. It is soluble in an ammoniacal solution of cupric oxide (see cupr-ammonia, p. 459), from which solution it may be precipitated by acids. It is not acted on by iodine. It is capable of fermentation, as shown in the ripening of fruits.

Concentrated alkaline solutions dissolve it slightly, converting it first into starch, and finally into gum ;—hence fabrics are injured by being boiled in soda. Heated with alkalies, it forms oxalic acid.

Action of Acids.—Dilute mineral and organic acids have very little action upon it. Hydrochloric acid dissolves it if the cellulin be heated with it, but the cellulin is precipitated on the addition of water. Sulphuric acid dissolves it, converting it first into dextrin, and finally after prolonged boiling in a quantity of water, into glucose. Nitric acid, (specific gravity, 1·2) has no action upon it unless the mixture be heated, when it forms oxalic acid.

Vegetable Parchment.—*Preparation.* By immersing blotting-paper in a mixture of 2 parts of oil of vitriol and 1 part of water. The paper after immersion needs thorough washing.

Properties.—Tough, waterproof, and transparent. It neither gains in weight nor alters in composition by the action of the acid, the change being molecular.

Gun-Cutton (*Pyroxylin; Nitro-cellulin; Cellulo-nitrin*).—*Preparation.* By soaking cotton wool in a mixture of fuming nitric (1·5 specific gravity) and sulphuric acids:—

$$C_6H_{10}O_5 + 3HNO_3 = C_6H_7(NO_2)_3O_5 + 3H_2O.$$

Cellulin + Nitric acid = Trinitro cellulin + Water.

Constitution.—Cellulin has been regarded as a trihydric alcohol $C_6H_7O_2(OH)_3$, and pyroxylin as a nitric ether, $C_6H_7O_2(NO_3)_3$; a similar relationship exists between glycerin, $C_3H_5(OH)_3$ and nitro-glycerin $C_3H_5(NO_3)_3$, and between ethylic alcohol, $C_2H_5(OH)$ and ethylic nitrate $C_2H_5(NO_3)$. The more rational formula for gun-cotton, however, seems to be $C_6H_7(NO_2)_3O_5$, *i.e.*, regarding it as a substitution product of cellulin, $C_6H_{10}O_5$, where H_3 has been replaced by $(NO_2)_3$.

Properties.—(*α.*) *Physical.* Notwithstanding that the form and appearance of the cellulin remains unaltered after the action of the acid, it will be found to have increased 82 per cent. in weight, and to have lost its power of depolarizing a ray of light. It will moreover, have become hygroscopic and highly electrical when rubbed or pulled out briskly. It is insoluble in alcohol, water, ether, or in dilute acids, but is soluble in acetic ether, in methylic acetate, and in a mixture of ether, ammonia, and potash.

(*β.*) *Chemical.* Its composition varies according to the strength of the acid employed :—

Thus, by the use of a less concentrated nitric acid, a less highly *nitrated* nitro-cellulin may be produced, such as the compounds $C_6H_9(NO_2)O_5$ and $C_6H_8(NO_2)_2O_5$, the latter constituting the dinitro-cellulin used for *collodion.*

Gun-cotton inflames at or about 400° F. (204·5° C.).

By the action of reducing agents (such as nascent hydrogen, etc.), gun-cotton may be reconverted into cellulin.

The products of its combustion are CO, CO_2, N, HNO_3, and CN.

Collodion is a solution of dinitro-cellulin in a mixture of alcohol and ether.

Uses of Cellulin.—In *nature*, its use is essentially vital, performing the functions of the plant, and elaborating the various products from the vegetable juices.

In the *arts*, cellulin is used in the manufacture of paper, cotton fabrics, gun-cotton, collodion, etc.

II. Woody Matter (*incrusting matter; sclerogen*). This is the deposit found either within the cell, or encrusting the cell wall. It is difficult to obtain it in a state of purity on account of the rapidity with which it becomes oxidized. It is insoluble in water, alcohol, or in ether. Unlike cellulin, it is soluble in alkalies. Exposed to the air, and more especially under the influence of certain parasitic plants, it becomes pulverulent ("*dry rot.*") Sulphuric acid does not, as in the case of cellulin, convert woody matter into sugar. Nitric acid tinges it yellow, and forms certain gelatinous compounds with it; hydrochloric acid renders it brown and black. Iodine with sulphuric acid turns it of a blue color. The products of its destructive distillation have been already described (page 597).

Uses.—In *nature* woody matter gives support to the plant. In the *arts* its uses are numberless.

III. Corky Matter is also an incrusting material, and always occurs outside the cell wall. The entire plant—leaves, fruit, flowers, and indeed every cell, is covered with it.

Properties.—It is lighter than, and impermeable to water. It is insoluble in water, in alcohol, or in ether. It is soluble in alkalies. It is insoluble in strong sulphuric acid except by heat, or after a prolonged period of action, but it is soluble in nitric acid (specific gravity, 1·2), which converts it into suberic acid. It is dissolved by chlorine. It is turned brown (not blue like woody matter) by iodine and sulphuric acid. It will not take a dye. These reactions show—

1. Why potatoes and fruits do not dry, *viz.*, owing to the impermeability to water of the corky, encrusting matter.
2. Why cotton must be first bleached with chlorine before being dyed, *viz.*, to remove the corky matter present on the cells.

Uses in nature.—To bind cells together, and to prevent the moisture in the cells evaporating.

The Life of a Plant.

The seed is placed in the ground.

The soil is formed by the combined action of air and rain containing carbonic acid in solution upon rocks. The water in the interstices of the rock, by expansion during a frost, assists in breaking down the rock upon which the rain and air have previously acted. Thus the soil derives certain *mineral* ingredients. The spores of the lower orders of plants, such as the lichens, find in the broken-down rock a resting-place, where they grow, live, and die; their remains supplying the soil with *organic* constituents necessary for the growth of plants of a higher order.

The seed is placed in this soil. Under the influence of warmth and moisture, and by the action upon it of a nitrogenized ferment (diastase), the *insoluble* starch of the seed is converted into *soluble* sugar, thus providing the first food of the plant, until it is able to shift for itself. The germ shoots, *i.e.*, sends forth leaves and roots. These are the organs whereby it obtains food, the former acting as lungs, or rather as organs of transpiration and formative organs, and the latter as mouths for the absorption of liquids necessary for its sustenance.

The food of the plant is entirely inorganic. To take the inorganic and to fit it for the use of the animal, is the special work of the vegetable. The ground on which the plant grows is the medium for such transference. One thing, however, is essential, *viz.*, that the food supplied to the plant should be soluble.

The leaves inhale ammonia and more particularly carbonic anhydride. The lower surface of the leaf is the active surface in this respect, as well as in the giving-off of the water absorbed by the roots. The leaves absorb but little water, a moist air being required in certain cases merely to check transpiration. Under the action of light and in the presence of water, the cells of the leaves fix the carbon of the carbonic anhydride, and exhale pure oxygen. This carbon they utilize in the preparation of the vegetable products characteristic of plant life.

The roots also take up—*carbon* as CO_2, derived from decaying organic matter, *nitrogen* from the ammonia carried down by rain or set free as a product of putrefaction, or derived from the nitrates and nitrites the results of nitrification, together with *sulphur*, *phosphorus*, and *chlorine* derived from the sulphates, phosphates, and chlorides in the soil.

Thus the plant grows, the tips of the buds and the extremities of the rootlets being the active points of growth. Here no starch is to be found, since in these parts it is converted into sugar to aid the growth.

The culminating point in the life of the plant is the formation of fruit. The unripe fruit, as well as fleshy roots and other vegetable organs, contain an insoluble body called *pectose*, to which the hardness of unripe fruits is due, together with a vegetable acid, such as citric, tartaric, malic, etc., to the presence of which their sour, rough and astringent taste is to be attributed. By the action of warmth, of the acid, and of a peculiar ferment present in the fruit (called by Frémy *pectase*) the insoluble *pectose* of unripe fruits undergoes change into the soluble *pectin* $(C_2H_3O_2)_n$ of ripe fruits, which, as ripening proceeds, becomes transformed into pectic and pectosic acids. These impart to the juice its power of gelatinizing (that is, of forming a jelly) when boiled. Further, the fruit as it ripens absorbs oxygen, and evolves carbonic acid. Thus the tartaric or other acid by oxidation becomes converted into fruit sugar. Thus—

$$\begin{array}{ccccccccc} 3C_4H_6O_6 & + & O_3 & = & C_6H_{12}O_6 & + & 3H_2O & + & 6CO_2. \\ \text{Tartaric acid} & + & \text{Oxygen} & = & \text{Fruit sugar} & + & \text{Water} & + & \text{Carbonic anhydride.} \end{array}$$

A similar change to that described above results in the case of the cellulin and of the starch by the assimilation of water.

Thus the ripe fruit becomes sweet.

The ripening action being complete, oxidation still continues, but it now induces the changes incident to decay.

Finally, the plant dies and decays. Its carbon is dissipated as CO_2, its hydrogen as H_2O, and its nitrogen as NH_3. Thus the dead plant becomes gaseous food for living plants. Its mineral constituents are washed into the soil, whilst its woody tissue rots and forms humus. These also serve as sources of food for fresh vegetation.

The plant-feeding power of the soil needs constant renewal in order to maintain its fertility. This is effected by manuring; phosphorus, sulphur, nitrogen and silica, together with lime, magnesia, and the alkalies, are supplied by gypsum (which, as well as supplying lime and sulphur, serves to retain the carbonate of ammonia by converting it into sulphate), by bone-ash, by superphosphate, by sodium chloride (which may be converted into carbonate, silicate, or other salts of sodium) by sodium nitrate, by the alkaline silicates (soluble silicates being needed more especially by the cereals), and by ammonium sulphate.

Further, dead plants, the ashes of plants, urine, solid animal excrement, guano (*i.e.*, the dung of carnivorous sea birds, which contains a large quantity of urate of ammonia), and soot which contains ammonia, are all employed as sources of food for the vegetable.

Sometimes the ground is allowed to lie fallow, chemical changes occurring in the soil by the action of air and moisture, whereby the ground becomes enriched.

The use of lime depends on its power of promoting the decay of organic, and the decomposition of mineral matters, whereby they are converted into soluble forms.

Lastly, it must be remembered that different plants, like different animals, need different foods. Hence the principle of " the rotation of crops."

CHAPTER XXXI.

ANIMAL CHEMISTRY.

ALBUMINOIDS: I. Animal Solids—II. Nutrient Fluids—III. Digestion, and the Fluids concerned in it—IV. Excrementitious Products.

ALBUMINOIDS OR PROTEIDS.

THE Proteids form the chief part of the solid constituents of every solid tissue, and are indissolubly connected with every manifestation of vital activity.

The formula $C_{72}H_{112}N_{18}O_{22}S$ represents their approximate composition. A little ash always remains after incineration, consisting chiefly of alkaline chlorides and phosphates.

Their *origin* is vegetable and vegetable only. It is the special work of the vegetable to form albuminoids out of the simple chemical compounds serving as their food.

The animal cannot form a proteid, but it can convert one proteid into another proteid characteristic of any special animal solid or fluid.

Their *end* is to be burnt up in the animal economy, the liver and kidneys being the main furnaces for such destruction. Water and carbonic acid, along with imperfectly oxidized organic bodies are formed as the products of the burning, these latter compounds containing the nitrogen of the proteid. Of such bodies, urea stands foremost. The processes whereby these compounds are formed are termed *metabolic processes.*

No doubt intermediate bodies are formed from the partial decomposition of the proteids prior to their ultimate destruction. Of such retrograde intermediate compounds, glycogen and fats are illustrations.

Whether proteids undergo higher synthetical development in the animal is doubtful. Possibly *hæmoglobin* may be an illustration of such higher development; but the process is at most unusual.

CLASSIFICATION OF THE PROTEIDS.

Class I. Albumens.

(Soluble in water. Solutions coagulated by heat.)

Name.	Source.	Properties.
Ser-albumen ..	Blood serum	A yellow, elastic, transparent body. If quite dry, may be heated to 100° C. without change. Its aqueous solution is precipitated by alcohol, and coagulated by heat. It is not precipitated from its solution by a small quantity of dilute acid, but is precipitated on the addition of acids in large quantity. The precipitate is soluble in excess of strong HCl, and in strong HNO_3. When injected into the veins, ser-albumen does not, like ov-albumen, pass into the urine.
Ov-albumen ..	Egg	Coagulated by ether and turpentine, which ser-albumen is not. It is also unlike ser-albumen in being insoluble in strong HNO_3. When injected into the veins, it passes into the urine unchanged.
Veget-albumen	Plants ..	Occurs in nearly all vegetable juices, especially in potatoes and wheat flour. Its reactions closely resemble those of ov-albumen.

Class II. Globulins.

(Insoluble in pure water. Soluble in dilute acids and alkalies, and in dilute solutions (1 per cent.) of NaCl or other neutral salt.)

Name.	Source.	Properties.
Myosin	Muscle ..	Coagulated by heat and by alcohol. Soluble in very dilute HCl, rapidly becoming acid-albumen or syntonin. Dissolves in dilute alkali, forming an *albuminate*.
Globulin (paraglobulin).	Prepared from *Blood serum*, by passing CO_2 through a dilute solution. *Aqueous humour.* *Crystalline lens.*	The globulin from blood serum is *fibrino-plastic*, *i.e.*, it can form fibrin in contact with certain bodies. In this respect it differs from the globulin of the crystalline lens. Precipitated by CO_2 or by very dilute acids from its solution in NaCl. Soluble in water saturated with oxygen, and in very dilute alkaline solutions; but if the solution contains 1 per cent. of alkali it dissolves as an albuminate, and not as free globulin. It is converted into acid-albumen by dilute acids. It coagulates at 158° F. (70° C.).
Fibrinogen ..	Pericardial fluid. Hydrocele fluid, etc.	Fibrinogen is more difficult to precipitate by CO_2, and less difficult to precipitate by a mixture of alcohol and ether, than globulin.
Vitellin	Yelk of egg	Vitellin is the residue left after treating the yelk with ether. It is a white granular body, insoluble in water, but soluble in solutions of neutral salts. It is neither fibrino-plastic nor fibrinogenous. It is converted into acid albumen by dilute acids, and is soluble in dilute alkalies as an albuminate. It is believed to be a mixture of albumin and casein.

Class III. Derived Albumens.

(Insoluble in water and in dilute NaCl solutions. Soluble in dilute acids and alkalies.)

Name.	Source.	Properties.
(*α*.) Acid albumen		Albumens dissolved in dilute acids. If the albumens of Class I. be acted on with a small quantity of dilute acid (HCl or acetic), the coagulation of the albumen does not take place at 70° C., and its levo-rotatory action on a polarized ray is largely increased (acid albumen). On carefully neutralising this acid solution, a white precipitate of albumen is thrown down, which will be found to be insoluble in water or in a sodium chloride solution, but to be soluble in an excess of an alkali or of an alkaline carbonate. Coagulates at 70° C. The albumens of Class II. are also soluble in dilute acids, forming acid albumens. The solutions yield a precipitate when neutralized, but this (unlike that produced in the case of Class I.) is not soluble in neutral saline solutions.
(*β*.) Alkali albumen (albuminate)		Albumens dissolved in dilute alkalies. Like acids, dilute alkalies prevent the coagulation of albumen by heat; but the albumen is precipitated on the solution being neutralized, precipitation not taking place in the presence of alkaline phosphates (albuminates).
Casein	Milk	Casein is closely allied to the artificial albuminates. It is coagulated by the action of certain animal membranes (rennet).
Plant casein (legumin) ..	Seeds of plants	Precipitated by rennet.

Class IV. Fibrin.

(Insoluble in pure water. Sparingly soluble in neutral saline solutions, or in dilute acids and alkalies.)

Name.	Source.	Properties.
Fibrin	Blood; lymph; chyle.	For its formation *see* Blood (pp. 808, 814). Fibrin is very elastic and possesses a filamentous structure. It is insoluble in water, except at very high temperatures, or after lengthened action. It swells up when acted on with dilute acids and alkalies, and dissolves slightly after their prolonged action, aided by heat. Swells up in cold HCl (1 per cent.), and dissolves with ease if pepsin be added to the acid solution.
Plant fibrin ..	Plants, especially seeds of cereals.	By boiling with sulphuric acid, is converted into leucine, tyrosine, and glutamic acid.

Class V. Coagulated Proteids.

(Insoluble either in dilute or strong acids, except acetic acid. Soluble in the gastric fluid (pepsin) or in the pancreatic juice (pancreatine), which converts the coagulated proteid first into *syntonin* and finally into *peptones*.)

Name.	Source.	Properties.
		Coagulated proteids are produced by the action of heat or of alcohol on neutral solutions of albumen, fibrin, myosin, etc. Strong HCl and also ether convert ov-albumen into a coagulated form. Heat similarly converts the albuminates into a coagulated form, but the precipitate may be reconverted into albuminates by potassic hydrate.

Class VI. Peptones.

(Bodies formed by the action of the gastric juice on albuminoids. Soluble in pure water ; solutions not being coagulated by heat. Insoluble in alcohol and ether.)

Name.	Source.	Properties.
Peptones ..	Stomach and small intestines only.	These bodies are highly diffusible. They are not precipitated either by acids or alkalies.

The proteids are amorphous colloidal substances, turning the plane of polarization to the left. Their solubilities are stated in the following table (from Fownes):—

I. Proteids soluble in water :

Aqueous solutions not coagulated by boiling	PEPTONES.
Aqueous solutions coagulated by boiling .	ALBUMENS.

II. Proteids insoluble in water :

(*a*.) Soluble in a 1 p. c. solution of sodic chloride	GLOBULINS.
(*β*.) Insoluble in a 1 p. c. solution of sodic chloride.	
Soluble in hydrochloric acid (0·1 p. c.) in the cold :	
Soluble in hot spirit	ALKALI-ALBUMEN.
Insoluble in hot spirit	ACID-ALBUMEN.

Insoluble in hydrochloric acid (0·1 p. c.) in the cold :	
Soluble in hydrochloric acid (0·1 p. c.) at 60° C.	Fibrin.
Insoluble in hydrochloric acid (0·1 p. c.) at 60° C. ; insoluble in strong acids :	
Soluble in gastric juice	Coagulated albumen.
Insoluble in gastric juice	Amyloïd.

Reactions of the Proteids.

1. The proteids are all soluble in acetic acid and in solutions of the caustic alkalies by the aid of heat. They coagulate, however, at different temperatures; albumens coagulating between 67° and 73° C., myosin below 55° C., whilst others require a temperature above 75° C.

Solutions of proteids react as follows :—

2. Precipitated on the addition of an excess of mineral acids.

3. A white precipitate produced by potassium ferrocyanide in an acetic acid solution.

4. Precipitated when an acetic acid solution is boiled with a saturated solution of sodium sulphate.

[Precipitation of a proteid occurs with basic lead acetate — with mercuric chloride—with tannic acid—with alcohol—also on the addition of powdered potassium carbonate to saturation, etc.]

5. *Millon's test* (Millon's reagent :—Dissolve mercury by heat in 2 parts of nitric acid ; dilute this acid liquid with twice its bulk of water. Pour off the clear supernatant liquid for use). A precipitate of a purple red colour is formed when a proteid is heated with Millon's reagent.

6. *Xanthoproteic reaction.*—Nitric acid and heat—Solution becomes yellow. — An amber-red color is produced on adding an excess of alkali to the yellow mixture.

A.—ANIMAL SOLIDS.

I ES, TEETH, SHELLS, ETC., FLESH, GELATIN, CHONDRIN, HAIR, SILK, BRAIN AND NERVE TISSUE.

Bone, Teeth, Shells.

TABLE I.

Composition of the Healthy Human Bones of a Child and of an Adult.

	Bones from a child æt. 13 months. Cause of death bronchitis.						Bones from a male æt. 40 years. Cause of death bronchitis.					
	Femur.	Tibia.	Fibula.	Humerus.	Radius.	Ulna.	Femur.	Tibia.	Fibula.	Humerus.	Radius.	Ulna.
C n ph ate fl e.	39·6	47·5	47·6	50·6	45·1	49·2	60·2	57·9	57·4	61·8	57 4	58·2
C n car te.	6·0	6·0	5·9	7·1	5·0	6·4	8·0	7·8	7·5	8·8	7·3	7·8
Mag um ph te.	1·0	0·8	0·8	1·0	1·0	0·8	1·4	1·4	1·3	1·4	1·3	1·6
A l m .	43·4	45·7	45·7	41·3	48·9	43·6	30·4	32·9	33·8	28·0	34·0	32·4

TABLE II.

Composition of the Bones of different Mammals, Birds, Fish, and Reptiles.

	Mammals (Femur of).							Birds (Femur of).		Fish (Vertebræ of.)		Reptile (Femur)
	Human æt. 40.	Sheep æt. 4.	Bull æt. 4.	Horse æt. 6.	Wild Boar.	Wolf.	Bat.	Thrush.	Sparrow.	Cod.	Salmon.	Rana Esculenta.
C n pho te.	58·0	55·9	54·1	54·4	58·9	57·9	57·5	58·6	59·5	57·6	36·6	59·5
C n flu e.	2·2											
C n car te.	8·0	12·2	12·7	12·0	9·0	11·1	4·8	5·1	8·9	4·9	1·0	2·2
Mag m pho te.	1·4	1·0	1·4	1·9	1·2	1·1	1·0	0·8	1·0	2·3	0·7	1·0
C s	..	0·5	0·8	0·7	0·9	1·0	0·7	0·8	0·9	1·0	0·8	1·8
A l m .	30·4	30·4	31·0	31·0	30·0	28·9	36·0	34·7	29·7	34·2	60·9	35·5

TABLE III.

Composition of certain Diseased Bones, of Teeth, and of various Shells.

	Diseased Bone.		Tooth.	Enamel of Tooth.	Crab Shell.	Oyster Shell.	Hen's Egg Shell.	Fish Scales (Perch).
	Rachitis. Tibia.	Caries. Femur.						
Calcium phosphate	26·9	38·4	64·3	88·5	6·0	1·2	1·0	37·8
Calcium fluoride..								
Calcium carbonate	4·9	5·4	5·3	8·0	62·8	98·3	97·0	3·0
Magnesium phosphate	0·8	1·1	1·0	1·5	1·0	..	..	0·9
Other salts	1·1	0·9	1·4	..	1·6	..	..	..
Animal matter ..	66·3	54·2	28·0	2·0	28·6	0·5	2·0	57·4

Omitting the periosteum, or external membrane of the bone, and the internal membranes, marrow, etc., bone consists of a mixture of an organic substance, called ossein, with certain inorganic compounds. It has been stated that iron has been found in bone, but this is probably due to the retention of a small quantity of blood in the bone.

We would note that:—

(1.) There is a close resemblance in the chemical composition of the bones of the higher mammalia. (Table II.)

(2.) The bones of the young contain more animal matter, and less earthy matter than the bones of adults. There is, however, no well-marked gradation in the proportions. (Table I.)

(3.) The composition of bone is influenced by certain diseases. (Table III.) These alterations consist generally in a diminution of the several earthy constituents.

(4.) The composition of bone varies slightly with the part from which it is derived. Thus the femur and humerus contain, as a rule, more earthy matter than the tibia and fibula or the radius and ulna of the same individual, whilst the scapula, the sternum and the vertebræ contain less earthy matter than the long bones. (*See* Table I.)

(5.) It would seem that the bones of males contain slightly more earthy matter than the bones of females.

Of other animal substances closely allied to bone we note—

(*a.*) **Teeth** (Table III.). The substance of the teeth is (excepting the enamel) very like bone in composition. The enamel (*i.e.*, the covering of the tooth external to the gum), is remarkable for containing very little organic matter and a large excess of inorganic constituents.

(*β.*) **The Shells** of the crustaceæ and of the mollusca, and also birds' eggs, contain generally but little phosphate and a considerable excess of carbonate of lime.

(γ.) In **Fish Scales** the phosphate of lime is less, and the animal matter more, than occurs in bone.

Properties of bone.

(α.) *Action of heat in open vessels.* The organic matter burns away, leaving a white "bone-ash" ($Ca_3P_2O_8$). This residue is used in the manufacture of phosphorus (*see* page 151), and for a manure principally in the form of superphosphate.

(β.) *Action of heat in closed vessels* (Destructive distillation). Ammonia and tarry matters (*Bone-oil* or *Dippel's oil*) are evolved, the residue remaining in the retort constituting "*Animal Charcoal*" or "*Bone Black.*" This consists of a mixture of phosphate of lime and finely divided carbon. Animal charcoal is largely used in sugar refining. After its decolorizing power has been exhausted, the charcoal may be burnt for the purpose of recovering the bone ash.

(γ.) *Action of water.* When bones are boiled in water at 212° F. (100° C.) all that occurs is the separation of the fat present in the bone. This floats on the surface of the water, the ossein of the bone being insoluble. If the bone, however, be digested in water at a temperature of 300° F., *e.g.*, in a Papin's digester, the organic matter is rapidly converted into gelatin, which is soluble in water. This converted ossein is used for glue.

(δ.) *Action of acids.* When dilute hydrochloric acid is added to bone, effervescence first occurs by the action of the acid on the lime carbonate. In time the dilute acid dissolves out the whole of the earthy phosphates, etc., leaving a semi-transparent horn-like body, called ossein (the organic constituent of the bone), which by the action of heat under pressure may be converted into gelatin.

(ε.) *Action of burial.* After long burial the organic matter of bone disappears, the inorganic constituents only remaining.

Flesh.

Composition of Flesh—

Water	78·0
Fibrin (with nerve tissue, blood-vessels, etc.).	17·0
Albumen	2·5
Other constituents of the juice	2·5
	100·0

Muscle contains about three-fourths its weight of liquid. One part of the water of muscle is due to the blood present, and a second part to the "*juice of flesh,*" as it is called, *i.e.*, an acid liquid containing kreatin, inosite, and certain salts, together with phosphoric, lactic, and butyric acids.

Kreatine ($C_4H_9N_3O_2 + aq$), when boiled in an acid, loses water and becomes *kreatinine* ($C_4H_7N_3O$), a minute trace of which is found in urine. When boiled with alkalies, kreatin gains water and yields *urea* (CH_4N_2O) and *sarcosin* ($C_3H_7NO_2$).

Inosite or *muscle sugar* ($C_6H_{12}O_6 + 2aq$), a body similar in composition but dissimilar in properties to grape sugar, may be prepared from the concentrated extract of flesh. It may also be obtained from green kidney-beans.

As soda is the chief alkali of the blood, the alkalinity of blood being supposed to be due to phosphate of soda (Na_2HPO_4), so potash is the chief alkali of the juice of flesh, the acidity of flesh being supposed to be due to the acid phosphate of potash (KH_2PO_4).

Gelatin and **Chondrin** do not pre-exist in the animal kingdom, but result from the action of boiling water on gelatinous tissues, such as skin, tendons and bones, or on chondrin-producing tissues, such as the cartilages of the ribs and joints.

Ultimate Composition of Gelatin and Chondrin.

	Gelatin.	Chondrin.
Carbon	50·0	49·1
Hydrogen	6·6	7·1
Nitrogen	18·3	14·4
Oxygen	25·1	29·4
	100·0	100·0

In addition to the above, earthy phosphates are always present in gelatin and chondrin.

Gelatin is found in a pure state as *isinglass* (the dried swimming-bladder of the sturgeon), and in a less pure state as calf's-foot jelly, glue, and size. It is soluble in hot water, but insoluble either in cold water, in alcohol, or in ether. It shrinks greatly in bulk when exposed to dry air. If perfectly dry, gelatin may be preserved indefinitely, but when moist it rapidly becomes acid, and putrefies.

A gelatin solution is precipitated as tanno-gelatin by tannic acid * (the only acid known that possesses the power of precipitating it), by alcohol, by mercuric chloride, by mercurous and mercuric nitrates, and by chlorine (as a chlorite of gelatine). It is neither precipitated by alum nor by basic or neutral lead acetate.

Boiled with strong alkaline solutions, it is converted into *leucine*, or *amido caproic acid* ($C_2H_{13}NO_2$), and *glycocol* (glycocine) or *amido-acetic acid* ($C_2H_5NO_2$), with the evolution of ammonia.

A one per cent. solution of gelatin sets on cooling. Repeated boiling destroys this property.

Chondrin is the gelatin obtained by the action of boiling water on the cartilages of the ribs and joints.

---

* Leather consists of a combination of a gelatinous tissue (as skin) with tannin (*see* page 736).

It is not so soluble as gelatin in boiling water. It is precipitated by acids. In the case of acetic acid the precipitate is insoluble in an excess of acid, but in the case of the other acids the least excess of acid effects the solution of the precipitate. Its solution is precipitated by alum and by lead acetate. It forms glucose when boiled with hydrochloric acid.

Uses.—*Size* is the gelatinized solution produced by boiling clippings of hides, parchment, etc., in water.

Glue is manufactured by boiling the parings of hides, etc., in water. The hides are first carefully cleansed from hair and blood by lime. This done, the lime is carbonated by free exposure, after which the hides are boiled in water. The liquid is kept warm for a time to allow the impurities to subside. The solution is then cooled, the gelatinized mass being cut into slices and dried on nets in the air. The temperature at which the drying process is effected is important, a summer heat having a tendency to melt the glue, and a winter cold to split it.

Hair contains 3 to 5 per cent. of sulphur.

Silk.—This is said to consist of three layers, the *outer* one of *gelatin*, and soluble in water ; the *centre* one of *albumen*, and soluble in boiling acetic acid ; the *inner* one of *sericin* ($C_{15}H_{25}N_5O_8$) and insoluble either in water or in acetic acid.

Brain and Nerve Tissue.—The *watery* extract (75 to 80 per cent.) of brain tissue contains inosite, kreatin, uric acid, xanthin, sarcine, and lactic acid, whilst the *solid undissolved matters* consist of fats, cholesterin, cerebrin or cerebric acid ($C_{17}H_{33}NO_3$) and lecithin ($C_{42}H_{84}NPO_9$). Lecithin is also found in the yolk of eggs, and is a substance largely diffused in the animal organism. It presents the appearance of a waxy mass, forming an emulsion with water, and uniting both with acids and bases. On boiling with acids, lecithin is resolved into choline, glycerophosphoric acid, palmitic and oleic acids. The ash (3 to 4 per cent.) consists mainly of the salts (especially potassium salts) of sulphuric and phosphoric acids.

B.—NUTRIENT ANIMAL FLUIDS.

BLOOD, CHYLE, LYMPH, MILK.

Blood.

Composition.—This can only be stated very generally, although it is to be remarked that the composition of blood is singularly uniform. This is the more remarkable, considering the work it has to perform in supplying the materials for the replenishment of worn-out tissue, and in carrying away some of the products arising from their destruction.

Average Composition per 1,000 *parts of Human Blood* (Becquerel and Rodier).

The quantities are stated in parts per 1,000 of blood.		Male.		Female.	
Specific Gravity of defibrinated blood			1060·0		1057·5
Do. of serum			1028·0		1027·4
Water			779·00		791·10
Fibrin (?)			2·20		2·20
Fatty matters.	Saponified fat	1·60	1·00	1·61	1·04
	Phosphorized fat		0·49		0·46
	Cholesterin		0·09		0· 9
	Serolin		0·02		0·02
Albumen			69·40		70·50
Blood corpuscles			141·10		127·20
Extractive matters and salts			6·80		7·40
			1,000·10		1,000·01
Salts	Sodium chloride	5·93	3·10	7·15	3·90
	Earthy phosphates		0·33		0·35
	Soluble salts other than NaCl		2·50		2·90
Iron			0·57		0·54

It may be noted that arterial blood contains more fibrin and less fat and albumen than venous blood.

The gases present in blood have been estimated by Magnus and Meyer.

Free Gases present in 100 *vols. of Blood taken from the Carotid of a Dog.* (*Corrected to* 0° C. *and* 760 *mm.*)

	Exp. 1.	Exp. 2.
Oxygen (free or combined with hæmoglobin)	12·43	14·29
Nitrogen	2·83	5·04
Free carbonic anhydride	5·62	6·17
	20·88	25·50

The *combined* carbonic acid was found to be, in 100 volumes of blood, in the first experiment, 28·61 volumes, and in the second experiment, 28·58 volumes. This would give a total of 49·49 and 54·08 volumes of gas, free and combined, in 100 volumes of blood. *Relatively* venous contains more carbonic acid and less oxygen than arterial blood; but *absolutely,* the carbonic acid, both in arterial and in venous blood, is always in excess of the oxygen.

Constitution.—Fresh blood, as revealed by the microscope, consists of numerous red globules (*blood corpuscles*) and of a few colorless corpuscles floating in a colorless liquid. This colorless liquid, termed the *liquor sanguinis,* consists of what is called blood serum, holding the fibrin, or fibrin-forming bodies, in solution. The composition of the blood corpuscles and of the liquor sanguinis respectively, are stated in the following table :—

Average Composition per 1,000 *parts of Blood Corpuscles and of Liquor Sanguinis* (*Serum and Fibrin*).

Blood corpuscles [Sp. Gr. 1088·5].		Liquor Sanguinis [Sp. Gr. 1028].	
Water	688·00	Water	902·90
Solid constituents	312·00	Solid constituents	97·10
Consisting of—		*Consisting of*—	
Globulin and cell membrane, or *stroma*	282·22	Albumen	78·84
Hæmatin *(with iron)* [This body is a derivative of hæmoglobin.]	16·75	Fibrin (?)	4.05
Fat	2·31	Fat	1·72
Extractive matters	2·60	Extractive matters	3·94
Mineral matter *(without iron)*	8·12	Mineral matter	8·55
Consisting of—		*Consisting of*—	
Chlorine	1·686	Chlorine	3·644
Sulphuric acid	0·066	Sulphuric acid	0·115
Phosphoric acid	1·134	Phosphoric acid	0·191
Phosphate of lime	0·114	Phosphate of lime	0·311
,, ,, magnesia	0·073	,, ,, magnesia	0·222
Potassium	3·328	Potassium	0·323
Sodium	1·052	Sodium	3·341
Oxygen	0·667	Oxygen	0·403

I.—*The Blood considered generally.*

Properties.—(*a.*) *Sensible and Physical.* The blood is a viscid, red fluid. As regards *color*, we have already noted that this is dependent on the presence of red corpuscles, and not upon any dissolved coloring matter in the liquor sanguinis. The exact color of the blood varies :—

(1.) It differs according to its source. Thus : the blood in the arteries, in the pulmonary veins, and on the left side of the heart, is of a florid scarlet red, whilst that in the veins, on the right side of the heart, and in the pulmonary arteries, is dull purple. This difference of color was at one time supposed to be physical, and due to alterations in the capacity of the red corpuscles (dependent on change of shape) for reflecting and transmitting light. It is, no doubt, true that the more spherical the globules, in other words, the more swollen the corpuscles are with water, the darker colored is the blood. Hence it was taught that carbonic acid effected the expansion of the cells, thereby rendering them bi-convex, and the blood dark ; whilst oxygen effected the contraction of the cells, thereby rendering them bi-concave, and the blood bright red. It is, however, tolerably evident that the color changes are not simply physical but chemical, and dependent on the state of oxidation of the hæmoglobin or blood-coloring matter. Thus, in arterial blood the hæmoglobin is oxidized, and of a scarlet color; whilst in venous blood a part at least of the hæmoglobin will be deoxidized, and purple. Possibly, the physical condition of the corpuscles, as well as the presence of carbonic acid, may be elements in the case; nevertheless, there can be but little doubt that the changes of color, from scarlet to purple and back again to scarlet, are primarily, if not entirely, due to the oxidation and deoxidation of the hæmoglobin.

(2.) The quantity of hæmoglobin in the corpuscles, as well as the proportion of corpuscles to serum, influences the color of the blood.

(3.) The form of the corpuscles (*see above*). Thus the more spherical the corpuscles, the darker the blood will appear.

(4.) The thickness of the cell-wall of the corpuscles. Mulder supposed this to be the real cause of the different colors of venous and arterial blood. He pointed out that potassium nitrate and iodide, and also sodium phosphate and carbonate, thicken the external membrane of the corpuscles, and render the blood of a lighter color.

(5.) Any reagents, like the caustic alkalies and certain organic acids, that burst the corpuscles, render the blood of a brownish-red color.

The *odor* of blood is more marked after it has been warmed. By treating the blood with sulphuric acid, its odor becomes so characteristic that it is often possible to say the animal from which the blood so treated was derived. (Barruel.) The odor of the blood of males is more intense and well-marked than that of females. This odor is supposed to be due to a volatile fatty acid.

Specific Gravity.—The specific gravity of living blood cannot be obtained. The blood first drawn has a higher (?) specific gravity than that drawn after an interval, owing to hæmorrhage increasing the quantity of water in the blood. Normal blood has a specific gravity varying from 1052·0 to 1057·0, 1055 being an average. Perfect health is, however, consistent with still greater variations than those mentioned. The specific gravity of the blood of women, and especially of pregnant women, is less than that of men, whilst it is least of all in children. The specific gravity of venous blood is always somewhat higher than that of arterial. The blood from various animals, so far as specific gravity is concerned, varies very little. The blood of the bullock (four experiments) was found to have an average specific gravity of 1060·0, whilst that of the sheep (seven experiments), was 1053·0. (Tidy.)

The *temperature* of the blood is usually 100° F. (37·8° C.), but the blood on the left side of the heart is said to be 1° to 2° F. (·55° to 1·1° C.) warmer than the blood on the right side. The blood is said to be warmed by passing through the liver, and cooled by its passage through the superficial capillaries.

(*β.*) *Chemical.* The blood has invariably a slightly alkaline reaction when first drawn from the body, but it becomes acid after a short time, owing, it is supposed, to the conversion of the sugar into lactic acid. Menstrual blood is said to be acid, but this is probably due to its intermixture with the acid mucus of the uterus or vagina.

Coagulation.—In from two to six minutes after the blood has been drawn from the body it *coagulates*, becoming in the first instance a red jelly-like mass, which becomes gelatinous after seven to fourteen minutes. Coagulation commences on the surface and near the sides of the vessel. The solid mass formed gradually *contracts*, forcing out a watery fluid. This stage of contraction, (*i.e.*, the separation of the *clot* or *crassamentum* from the *serum*) is usually complete in from twelve to forty hours. The "*clot*" consists of fibrin with the blood corpuscles entangled in its meshes (the blood corpuscles not having had time to subside before coagulation), whilst the "*serum*" is the liquor sanguinis *minus* the fibrin, and in which the clot floats.

If from any cause the clot contracts less rapidly than usual (as happens in inflammatory blood, and normally in horses' and donkeys' blood), or if the red corpuscles sink more rapidly than usual, owing to a greater tendency of the blood corpuscles to form rouleaux (as happens in inflammation), or to a relative deficiency of red corpuscles (as in chlorosis) a white layer collects on the surface of the clot, consisting either of fibrin only, or of a mixture of fibrin with white corpuscles. This constitutes what is called the "buffy coat," or the "inflammatory crust" of blood. This "buffy coat" contracts more rapidly than the rest of the clot. Hence a cupped depression on the surface of the clot becomes apparent after a short time.

The earlier physiologists explained the coagulation of the blood in a variety of ways :—(1.) By some (*e.g.*, by Borelli) it was thought that the liquidity of the blood depended on its constant motion, whilst coagulation resulted from want of movement. (2.) By others, coagulation was supposed to depend on the action of the air. This theory was upset since it was found that coagulation took place in vacuo. (3.) By others, coagulation was traced to the cooling of the blood. Experiments however, on the contrary, indicated that the temperature of the body was in reality that most favorable to coagulation. (4.) By others (John Hunter) coagulation was supposed to be due to the action of life, being connected, according to their theory, with the vitality of the blood.

Hewson was the first to suggest that coagulation depended on the separation of some one or more solid constituents from the liquor sanguinis.

Buchanan first noted that ascitic and hydrocele fluids, etc., did not coagulate spontaneously, but that so soon as a little of the liquid pressed from a blood clot had been added to these fluids a coagulum was formed, coagulation in such case being similar to that occurring in blood;—in other words, Buchanan showed that the liquid from a "washed blood clot" would coagulate liquids otherwise non-coagulable.

This action, it was proved, did not depend, as was suggested in the first instance, on the blood-coloring matter. Buchanan concluded that fibrin did not coagulate spontaneously any more than casein or albumen, but that its coagulation in the blood depended on the presence of a second substance, which, by its action upon the fibrin, occasioned coagulation. In fact, he urged that just as rennet coagulated casein, so this second substance, whatever it was, coagulated fibrin.

What, then, was this coagulating material? The washed blood clot (he remarked) consisted of fibrin and colorless blood corpuscles. Buchanan believed the colorless blood corpuscles to be the active agents of coagulation. In support of this view he urged (1) that the buffy coat of horses' blood was one of the most powerful coagulating agents, preserving its energy even after it had been dried and pulverized; and (2) that the *upper* layers of the red clot were more active than the lower layers. In both these cases it was noteworthy that the colorless blood corpuscles were specially numerous.

Buchanan's views amounted to this: "That coagulation depended on some one or more soluble constituents of the liquor sanguinis becoming insoluble fibrin by the action exerted upon it or them by the colorless corpuscles."

The next question he investigated was, What is the nature of the soluble body on which the white corpuscles act? Some authorities urged that it was soluble fibrin; others (as Denis, in 1859) that it was a proteid body (to which the name *plasmine* was given), yielding fibrin as the result of its decomposition, together with another proteid soluble in the serum.

Schmidt's researches indicated that two distinct substances were present in blood, to which he gave the names *fibrinogen* and *paraglobulin.* He held that the *paraglobulin* (a fibrinoplastic body) by its action on the fibrinogen occasioned coagulation. Coagulation was complete so soon as all the fibrinogen had been thus converted. But after complete coagulation, there remained, he said, an excess of paraglobulin. Ascitic fluid (he argued) contains no paraglobulin, but much fibrinogen. The fluid from the washed blood clot, containing some of the excess of the paraglobulin of the blood, was capable, therefore, of coagulating the fibrinogen of the ascitic fluid. Hence the reason, according to this view, (1) that blood coagulates spontaneously, *viz.*, because it contains both fibrinogen and paraglobulin; (2) that ascitic fluid does not coagulate spontaneously, *viz.*, because although it contains fibrinogen, it does not contain paraglobulin; and (3) that ascitic fluid does coagulate if the liquid from a blood clot be added to it, *viz.*, because the fluid of the washed blood clot contains some of the excess of the paraglobulin present in the blood, but absent in the ascitic fluid.

Paraglobulin, according to Schmidt, up to this period, was a fibrin ferment. If a fluid containing fibrinogen did not coagulate, its inability to coagulate depended on the absence of the fibrin ferment, paraglobulin. The next fact, however, clearly made out was that in certain fluids both fibrinogen and paraglobulin were present, and yet that they would not coagulate unless a little blood serum was first added to them. It appeared certain, therefore, that the fibrin ferment was some substance other than either fibrinogen or paraglobulin. Schmidt found that this fibrin ferment might be dissolved out of the blood serum by the prolonged action of alcohol, a re-agent which coagulates proteid matters. Notwithstanding that this fibrin ferment was proved not to exist in fresh blood, a variety of facts connected the ferment with the colorless blood corpuscles. Later experiments indicated that for these corpuscles to act as a ferment they must have undergone a destructive or breaking-down process : in other words, that fibrin results from the action of a fibrin ferment (formed within the colorless blood cells, but not set free until the cells become disintegrated) on fibrinogen, a proteid body present in blood serum.

The energy of coagulation seems to depend on the amount of fibrin ferment present.

Schmidt regards the presence of paraglobulin (as well as of fibrinogen) to be essential to coagulation, whilst Buchanan and Hammerston consider the presence or absence of paraglobulin to be immaterial.

Dr. Wooldridge, whilst accepting the view that the fibrin ferment may be derived from the cellular elements of blood, considers that it may also make its appearance in a blood plasma that has been freed from cellular, and, indeed, from all formed elements, in which case it must arise, he contends, from some constituent or constituents of the plasma itself.

Coagulation is influenced by a variety of circumstances :—

(1.) *The Origin of the Blood.*—Women's blood coagulates more rapidly than the blood of men, but the clot is less firm. Embryonic blood coagulates imperfectly. Arterial blood coagulates more rapidly than venous.

(2.) A warmth above that of the human body, such as 100° to 120° F. (37·8° to 54·0° C.), promotes coagulation. A higher temperature than this retards it, whilst a temperature of 200° F. (93·3° C.) stops coagulation altogether, even after the blood has been again cooled. Conversely, a cold of 40° F. (4·5° C.) entirely stops coagulation (Davy) ; but the power to coagulate under these circumstances is not destroyed, but takes place as well as ever after the normal temperature of the blood has been restored.

(3.) Motion retards coagulation, but rest promotes it.

(4.) The multiplication of points of contact promotes coagulation. Thus blood coagulates more rapidly in a small, narrow vessel than in a wide one. It is customary to whip blood with a bundle of twigs to coagulate the fibrin. Or, again, the blood coagulates more rapidly in the rough cavities of the heart than in the smooth veins and arteries. After somatic death the blood remains liquid for some time in all the vessels, except in the heart and principal trunks, *provided the vessels are healthy.*

(5.) Contact with living tissue retards coagulation, whilst contact with foreign or dead tissue favours it (Hunter, Hewson). Thus we pass a thread through an aneurism to form a nucleus for coagulation, and so assist the cure.

(6.) The addition of two parts of water to one of blood promotes coagulation (Hunter, Prater), but the admixture of a greater quantity of water than this, retards it.

(7.) Free access of air promotes, whilst exclusion of air retards coagulation.

(8.) Coagulation is either retarded, or entirely prevented, by the presence of the alkaline hydrates, carbonates, and acetates; also by dilute acids; also by potassium or calcium nitrates, by ammonium and sodium chlorides, and other neutral salts, etc.

(9.) Coagulation is influenced by the mode of death. Thus in death by asphyxia, where the blood is imperfectly aërated, coagulation is retarded. According to Hunter, the same result occurs after death from lightning, blows on the stomach, over-exertion, fits of anger, etc.

(10.) The consistency of the blood clot depends mainly on the quantity of fibrinogen present in the blood.

The blood consists, as we have said, of corpuscles and serum, in the following proportion, according to Schmidt, per 1,000 parts :—

	Man.	Woman.	Dog.
Moist corpuscles	513·02	396·24	543·56
Serum	486·98	603·76	456·44

II. *The Blood Corpuscles.*

The composition of the blood corpuscles has been already stated page 805). These corpuscles are of two kinds, red and white.

1. *The White Corpuscles.*—These are present in blood in the proportion, in health, of 1 white to 400 or 500 red. This proportion, however, is greatly influenced (*α.*) *by food,* the quantity of white corpuscles being decreased in number by fasting, but increasing half an hour after food has been taken, the increase continuing, on an average, for a period of two hours; and also (*β.*) *by disease,* the quantity being greater than normal in pneumonia, tuberculosis, and more especially in

leucocythemia. (γ.) Moreover, in the blood of certain portions of the body, as in that of the spleen, the relative proportion of white corpuscles to red is greater than in other parts.

The white corpuscles are circular and nearly spherical. They have the power of assuming various irregular forms, known as their "amæboid movements." They are about $\frac{1}{2500}$ of an inch in diameter. They are specifically lighter than the red corpuscles, and contain neither fat nor hæmoglobin.

2. *The Red Corpuscles.*—These are red, circular, flattened discs, having an average diameter of $\frac{1}{1000}$ of an inch, and an average thickness of $\frac{1}{10000}$ of an inch. They are, relatively to the liquor sanguinis, fewer in women's blood than in men's, and in the blood of the old and young of all animals than in that of the middle-aged. Moreover, their proportions vary in the blood of different animals; *e.g.*, there are relatively a greater number of red corpuscles in the blood of birds than in the blood of carnivorous and herbivorous mammalia, whilst the proportion is smallest in the blood of cold-blooded animals. Lastly, the proportions vary in the blood of different vessels. Thus there are relatively fewer in arterial than in venous blood, fewer in the portal vein than in the jugular, whilst they are most abundant of all in the hepatic. The quantity, moreover, in the blood is *diminished* by want of food, by repeated bleedings, etc. Diminution of red corpuscles has also been noted in certain diseases, such as diarrhœa, intermittent fever, chlorosis, affections of the brain, etc. The quantity is *increased* by a fat diet, and in such diseases as cholera, spinal irritation, the early stages of heart-disease, general plethora, etc.

Constitution and Properties of the Red Corpuscles.—The red corpuscle is a non-nucleated body. It is not a cell, in the sense of a sac. It consists of a tough, elastic, transparent framework, or *stroma* (that is, not merely a cell-wall), infiltrated with a fluid containing globulin (an albuminous body), and a red coloring matter, called hæmoglobin. A little fatty matter, iron, and other mineral constituents are also present. The central light or dark spot seen with the microscope depends on the unequal refraction of transmitted light.

The red corpuscles have an average specific gravity of 1·088, but this is influenced materially by disease. In a case of cholera, the corpuscles were found to have a specific gravity of 1·102. Inasmuch as the specific gravity of water is less than that of the fluid contents of the corpuscle, it follows that, when mixed with the corpuscles, it will pass by osmosis into the cell, swelling out, and if the action be allowed to continue long enough, finally bursting it.

We shall now consider the chemistry of some of the constituents of the corpuscle.

1. **Globulin** is a substance similar in composition to, and in its properties closely resembling, albumen. It is found in large quantity

(10 to 14 per cent.) in the crystalline lens, and for this reason has been called *crystallin.*

2. Hæmoglobin ($C_{600}H_{960}N_{154}FeS_3O_{179}$) (*hæmato-globulin; hæmato-crystallin*).—This is the true, and only coloring matter of the blood of vertebrate animals. Its percentage composition is stated as—

Carbon	54·2
Hydrogen	7·2
Nitrogen	16·0
Oxygen	21·5
Sulphur	0·7
Iron	0·4 = 100·00

Preparation.—(1.) By the action of cold water, in which the hæmoglobin is soluble, on the corpuscles.

(2.) If a drop of blood, placed on a glass slide, be diluted with water, alcohol, or ether, and after a short exposure to air be covered over with a thin glass slip, crystals of hæmoglobin will be formed and be apparent under the microscope. (Funke.)

Properties.—Hæmoglobin may be obtained from blood, in a crystalline form (Hæmato-crystallin of Funke).

The forms of hæmogoblin crystals vary according to the animal. Thus they are—

(*a.*) *Prismatic,* in the blood of fish, in human blood, and in the blood of most mammals.

(*β.*) *Tetrahedral,* in the blood of the rat, mouse, and guinea-pig.

(*γ.*) *Hexagonal,* in the blood of the squirrel.

The formation of hæmoglobin crystals is promoted by light, and by the chemical action of oxygen and carbonic acid on the corpuscles. It is specially to be noted that the crystals are not the result of the evaporation of the water of the blood, inasmuch as they are formed more readily when the blood is diluted with twice, than when only mixed with one-half, its volume of water.

Hæmoglobin is soluble in cold water, but not in hot. The prismatic crystals are soluble in 94 parts of cold water, the solution coagulating at 147·2° F. (64° C.), while the tetrahedral crystals are soluble in 600 parts of cold water, the solution coagulating at 145·4° F. (63° C.). This coagulation consists not merely in the coagulation of the albumen, but in the formation of hæmatin. Hæmoglobin decomposes peroxide of hydrogen like spongy platinum. The red solution of hæmoglobin is decolorized by chlorine, with the precipitation of white flakes (the *chlorhæmatin* of Mulder), and undergoes change to a brownish-red color by the action of carbonic oxide, and to a brown color by nitrogen. It may be said generally, that whatever precipitates, destroys hæmoglobin. The feeblest acids (even CO_2) decompose it.

Hæmoglobin gives an absorption spectrum of two bands (between D and E) in the yellow and green.

The remarkable property possessed by hæmoglobin of combining with and delivering up oxygen has been already referred to (*see* page 82).

Carbonic oxide displaces the oxygen of oxy-hæmoglobin to form, with the hæmoglobin, a *more stable compound*, which resists reducing agents. Hæmoglobin also combines with nitric oxide to form a compound of even greater stability than that it forms with carbonic oxide ; for just as CO displaces O, so NO will displace CO.

It is said that hydrocyanic acid combines with hæmoglobin, but this is doubtful.

A body, intermediate between hæmoglobin and hæmatin, called *hæmatoidin* (*methæmoglobin* or *methæmatin*) ($C_{14}H_{18}N_2O_3$, Robin), is said to be found in blood after its extravasation in the tissues of living animals ; also in the brown fluids of hydrocele, ovarian cysts, etc.

Hæmatin.— By the action of heat, of mineral and other acids, of alkalies, etc., hæmoglobin undergoes conversion into *hæmatin* (*hæmatosin*) [$C_{68}H_{70}N_8Fe_2O_{11}$, Hoppe]. This body, which contains 12·8 per cent. of iron oxide, was once supposed to be a constituent and the true coloring matter of the red corpuscles, but is now proved to be merely a product of the decomposition of the hæmoglobin.

Hæmatin is an amorphous, blackish-brown substance, without taste or odor. It is insoluble in water, alcohol, ether, or acetic ether. It is also insoluble in all oils, or even in concentrated mineral acids. It is soluble in alcohol acidulated with either sulphuric or hydrochloric acid, and in aqueous or alcoholic solutions of the alkalies or of their carbonates. The brown acid alcoholic solution, when treated with an alkali, appears red by reflected, and green by transmitted light. It is a body easy of reduction, but very difficult of oxidation. It is decomposed by chlorine, by boiling with nitric acid, etc.

Hæmatin Chloride; Teichmann's *Hæmin Crystals ; Blood Crystals.*

Preparation.—By acting on hæmoglobin with common salt and glacial acetic acid.

Properties.—Rhombic dichroic crystals, insoluble in water, alcohol, and ether, but soluble in acids and alkalies. Acetic and hydrochloric acids are, however, the only reagents that dissolve it without decomposition.

III.—*The Liquor Sanguinis, or Plasma.*

The composition of the liquor sanguinis has been already stated (page 805). By the term "serum" is meant the liquor sanguinis, *minus* the proteid body which forms fibrin.

Preparation.—If fresh uncoagulated blood be mixed with common salt, the corpuscles will be found to subside, and the liquor sanguinis may be filtered off or decanted. Like blood, liquor sanguinis coagulates, and in doing so follows much the same course.

Properties.—In health, a straw-colored, viscous fluid, becoming in certain diseases, such as icterus and pneumonia, of an intensely yellow color. Its specific gravity varies from 1·026 to 1·029, the average being 1·028. In this respect it is singularly uniform. Its reaction is *alkaline*, like blood, the alkalinity being due to the presence of carbonate and phosphate of soda.

[NOTE. — Serum is also straw-colored, alkaline, and usually transparent. It becomes milky after a full meal, the milkiness being due to finely divided fat, and is most manifest after an excess of fat has been eaten. It coagulates at 170° F. (76·1° C).]

1. Water.—The quantity of water in blood varies. Thus there is more water in the blood of women (especially during pregnancy) than in that of men, and more in those of advanced age than in the young. The proportion present is influenced by disease. Thus there is a great diminution in the quantity of water in the blood in cholera. Further, arterial blood contains more water than venous blood, whilst in both venous and arterial blood the actual proportion of water varies hourly with food, exercise, and atmospheric changes. Nevertheless, a remarkable uniformity is noticeable, for that which lessens the water excites thirst; whilst, if an excess of water be added to the blood, the urine and perspiration effect its removal.

2. Paraglobulin.—The nature of this body has been already discussed (page 808). It is precipitated from serum by magnesium sulphate.

3. Serum Albumen ($C_{72}H_{112}N_{18}SO_{22}$). The quantity varies from 60 to 70 parts per 1,000 of blood. Its presence is the cause of the coagulation of the serum when heated to 75° C. It may be obtained in a soluble state by the cautious evaporation of the serum at a temperature below 120° F. (48·9° C.) If the serum be evaporated at a high temperature, the albumen becomes insoluble in water at ordinary pressure.

Hoppe considers that the albumen is not dissolved in blood, but is present in a state of fine subdivision. Others believe it to be present as an albuminate of soda, whilst Enderlin believes it to be held in solution by the sodium phosphate. The blood of women contains more albumen than the blood of men, whilst arterial blood contains less albumen than venous. The quantity of albumen in the blood is decreased in certain diseases; *e.g.*, Bright's disease, scurvy, puerperal fever, etc., whilst it is increased in cholera, intermittent fever, etc.

4. Fibrin.—The proportion of fibrin, or of the proteid body forming the fibrin, in blood, varies between 2 and 3 parts per 1,000. There is said to be more fibrin in arterial than in venous blood. The quantity is usually increased in inflammatory affections, such as rheumatism, pneumonia, etc., and decreased in anæmic diseases, as typhus, chlorosis, etc. Its spontaneous and speedy coagulation distinguishes it from all analogous substances.

All muscular tissue consists of fibrin. The gluten of flour is often called vegetable fibrin, and bears a close resemblance to animal fibrin.

Preparation.—Fibrin may be obtained from blood by stirring with twigs, and afterwards washing to get rid of the red corpuscles. In this condition the fibrin is white, stringy, and elastic. To purify it, the dried mass should be powdered, and treated successively with (1) dilute hydrochloric acid, (2) alcohol, and (3) ether. But, even after this treatment, it always contains a certain small quantity of inorganic salts.

Fibrin differs from most proteids in that, when once formed, it is insoluble in pure water, although it has had neither heat applied to it, nor been acted upon by metallic salts.

Fibrin is soluble in water, and also in a solution of 1 part per 1,000 of HCl at 40° C., when it forms syntonin or acid albumen. It is also soluble in dilute ammonia, in KHO, or NaHO, at the temperature of the body, the solution being incapable of coagulation by heat, or by the action of metallic salts.

Fibrin decomposes peroxide of hydrogen, oxygen being set free. It becomes blue when treated with tincture of guiacum and a solution of peroxide of hydrogen, the color being dependent on the oxidation of the guiacum resin by the oxygen set free from the H_2O_2.

[For remarks on coagulation, *see* page 807.]

5. Fatty Matters.—The proportion of fat in blood is about 1·6 parts in 1,000. The quantity, although not increased beyond this amount by a fat diet, suffers decrease by a want of fat food. Arterial blood contains less fat than venous, and the blood of the portal vein more fat than that of the jugular. The quantity of fat (and especially of cholesterin) is increased at the commencement of every acute disease, and also in certain chronic diseases.

Most of the fatty matter present in the blood is in a saponified form. It would appear that the fats peculiar to various organs exist ready formed in the blood, as *e.g.* cholesterin (the fat of bile), cerebrin and the phosphorized fat of the brain, together with oleic, margaric and stearic acids, chiefly saponified, but also in a free state.

These fatty matters of the blood not only supply fat where it is needed, but serve by their oxidation to maintain the temperature of the body.

6. Extractive Matter.—By this term we include *kreatin* and *kreatinine*, *glucose*, *urea*, *uric acid*, *hippuric* and *lactic acids*, etc.

Alcohol is said to be always present in blood in minute quantity. It is supposed to be formed by the fermentation of the sugar. (Ford. Jahresb., 1861, page 792.)

6. Mineral Matters.—The percentage composition of the ash of the serum may be thus stated :—

Sodium chloride	61·08
Potassium chloride	4·08
Sodium carbonate (Na_2CO_3)	28·87
Hydric sodium phosphate (Na_2HPO_4) ...	3·19
Potassium sulphate	2·78 = 100·00

The proportion of mineral ingredients is greater in the blood of adults than in that of the young, and in arterial than in venous blood. The quantity of mineral matter in blood is influenced by diet and by disease. There is a larger quantity present in the blood of the cat, goat, and sheep than in the blood of men, birds, and pigs, whilst a smaller quantity is found in the blood of dogs and rabbits than in that of other animals.

The iron (a never-failing constituent of blood) belongs exclusively to the red corpuscles.

[For many details connected with blood, such as the measurements of the corpuscles, tests, etc., *see* Tidy and Woodman's "Handy Book of Forensic Medicine."]

Chyle and Lymph.

Chyle is the fluid of the *lacteals*, the lacteals being the lymphatics of the intestines. It is transparent when taken from the thoracic duct of a fasting animal, but of a milk-like appearance during digestion. This milkiness is due to the presence of minute fatty particles termed 'the molecular base' of the chyle.

Lymph is the fluid of the *lymphatics*. It is also found in those extra-vascular spaces from which the lymphatics originate. It is a clear, colorless, faintly alkaline, albuminous liquid, having no fatty particles such as are found in suspension in chyle.

Lymph is, in fact, dilute liquor sanguinis, deprived of certain of its constituents abstracted from it by the various organs, and augmented by other constituents, such as urea and the effete products of tissue metabolism.

In both lymph and chyle the presence of certain corpuscles, most of them being colorless, but a few colored, may be seen under the microscope, floating in a clear liquid (*the lymph plasma*). Both are alkaline liquids, having a salt taste, and a specific gravity varying from 1·012 to 1·022.

Percentage Composition of Lymph and Chyle (Owen Rees).

	Chyle.	Lymph.
Water	90·237	96·536
Albumen	3·516	1·200
Fibrin	0·370	0·120
Animal extractive	1·565	1·559
Fatty matter	3·601	A trace
Salts	0·711	0·585
Total	100·000	100·000

We remark—(1.) That lymph and chyle are substantially alike, except that chyle contains fat, and lymph none or nearly none. Their composition varies, because the different organs take what they severally require from the transuded fluid, and give back the products of their decomposition. Hence lymph must differ in its composition more or less according to situation and the functional activity of the organs contributing to it.

(2.) Lymph and chyle are substantially like blood, the difference being only one of degree. The proteids present are fibrinogen, a globulin, and serum albumen. In fact, these liquids probably are rudimental blood, containing corpuscles in course of development into red corpuscles. The difference between lymph and chyle and the blood becomes less and less as the two former pass through the thoracic duct; in other words, as they approach the place where they are to be mingled with the blood.

(3.) Blood, lymph, and chyle agree, in that they contain fibrin (the quantity in lymph and chyle being about one fourth that present in blood) and coagulate spontaneously in from three to twenty minutes, although the clot formed from lymph and chyle is softer than that formed from blood. Moreover, in this property of spontaneous coagulation, these three fluids differ from all other animal fluids.

Milk.

Milk is a liquid secreted by the female mammary gland after parturition. Microscopically, it consists of fat globules surrounded by an albuminous envelope, these fat cells having a diameter of 0·0014 in and floating in a perfectly transparent liquid.

Composition per 100 *parts of Human and Cow's Milk.*
(Tidy).

	Woman's Milk.			Cow's Milk.
	Max.	Min.	Average.	Average.
Casein..	4·36	2·97	3·52	3·64
Butter..	5·18	4·45	4·02	3·55
Sugar of milk	4·43	3·29	4·27	4·70
Various salts	0·23	0·38	0·28	0·81
Total solids	14·20	11·09	12·09	12·70
Water..	85·80	88·91	87·91	87·30
Total	100·00	100·00	100·00	100·00

Milk is a model diet. The casein is its nitrogenised constitutent, the fat, sugar, and mineral ingredients (the chief of which is phosphate of lime) of food, being duly represented.

An increased yield of milk in the animal is promoted up to a point by an increase in the quantity of albuminous and fatty elements taken as food, and *vice versâ.* A very fat diet increases the proportion of all the ingredients and not of the fat only.

Milk is a yellowish, sweet liquid. The cream after a short time collects on the surface, the lower part or "skimmed milk" (as it is called) increasing at the same time in specific gravity. If the cream be well agitated the albuminous envelopes burst, and the fat globules coalesce to form butter. The fatty matter of cream is chiefly olein, but it also contains stearin and butyrin (butyrate of glycerin).

The reaction of fresh milk is variously stated. It is probably nearly neutral or very slightly alkaline. After a time the milk becomes acid and then coagulates. This action is rapid if the weather be warm and the air electrical. It is occasioned by the conversion of the milk-sugar into lactic acid under the influence of the nitrogenized body casein, which acid effects the precipitation of the casein (lactic fermentation). The precipitated casein, containing the milk globules in mechanical admixture, constitutes "*curds*," the clear liquid being known as "*whey.*"

Normal milk contains no albumen, although colostrum (that is, the first milk secreted after pregnancy) usually abounds in it.

Human milk has an average specific gravity of 1030.

C.—DIGESTION AND THE FLUIDS CONCERNED IN IT.

Saliva; Gastric Juice; Pancreatic Fluid; Bile; Intestinal Juice.

Digestion is a process of solution, *i.e.*, of rinsing or drenching the food with various secretions in order to extract from it the nutritious portions, and to convey them into the circulation.

To carry out this rinsing process perfectly, the food is first, in most cases, cooked, and then chewed. In this way the more perfect admixture of the food with the various solutive agents is effected.

The following table represents the amount of the digestive fluids said to be secreted daily, and the proportions of their chief constituents:—

	Quantity Secreted.	Solid Matters.	Active Principles.
Saliva	3·53 lbs.	231 grs.	116 grs. of ptyalin.
Gastric juice	14·11 ,,	2,963 ,,	1,482 ,, of pepsin.
Pancreatic fluid ..	0·44 ,,	309 ,,	39 ,, of pancreatin.
Bile	3·53 ,,	1,234 ,,	1,058 ,, of organic ferment.
Intestinal mucus ..	0·44 ,,	46 ,,	28 ,, ,, ,,
Total	22·05 lbs.	4,783 grs.	2,723 grs. of special solvents.

Saliva.

Saliva is a fluid secreted by various glands, such as the parotid, submaxillary, sublingual, etc. Two to three pints may be taken as an average quantity secreted during twenty-four hours. The exact amount, however, varies considerably. The quantity secreted is decreased by fasting, and increased by the stimulus of food in the mouth, or, indeed, by the mere mental impression connected with the sight or even the thought of food.

Composition per 1,000 *parts of Saliva* (Frerichs).

Water	994·1		
Solids	5·9	Organic	3·61
		Inorganic	2·29

The organic constituents of saliva consist of an albuminoid substance called *ptyalin* (πτύω to spit) (constituting about one-fourth the total solid matter of the saliva), together with fat, epithelium, etc. The ptyalin is said to be contained more largely in the saliva secreted by the submaxillary than in that of the other salivary glands. The inorganic constituents consist of the phosphates of lime, magnesia, and soda (the deposition of the earthy phosphates on the teeth by the action of the ammonia of the breath constituting what is called "tartar"), of alkaline chlorides, and of a small but an ever-present quantity of potassium sulpho-cyanide, said to be increased if sulphur be taken internally.

Properties, &c.—Saliva is a clear, feebly alkaline fluid. Its specific gravity varies from 1002 to 1009. The alkalinity of the secretion from the parotid is said to be more marked than that from the other salivary glands. During digestion, moreover, the alkalinity of the saliva increases. In certain diseased conditions the saliva becomes distinctly acid.

The action of the saliva is twofold—

(α.) As a *mechanical agent*, it acts as a lubricator, assisting mastication and deglutition. In some animals this is its only function.

(β.) As a *chemical agent*, its action depends on the presence of the ferment body '*ptyalin*,' the insoluble starch being transformed under its influence, into soluble dextrin and glucose. This conversion of starch is retarded rather than promoted by the gastric juice. The saliva may also, being an alkaline fluid, assist in emulsifying the fat, but has no special action on fats or proteids. The action of saliva is hampered by the presence of the concentrated product of its own action (*viz.*, sugar).

Gastric Juice.

The gastric juice is a fluid secreted from the glands of the stomach, under the influence of disturbing causes, such as the introduction of food and other mechanical irritants, and more especially by soluble irritants, such as salt, etc. The quantity secreted in the twenty-four hours has been variously stated at from 10 to 20 pints.

Composition of Human Gastric Juice per 1,000 *parts.*

Water	994·4		
Solid constituents ...	5·6	Organic (pepsine) ...	3·2
		Inorganic	2·4

The salts present in the gastric fluid consist of calcium, sodium, and potassium chlorides, together with earthy phosphates.

The two important constituents of the gastric fluid are the free acid and the pepsin :—

(α.) As regards *the free acid*, some investigators have maintained it to be lactic acid, and others hydrochloric acid. M. Verneuil states that he has found both acids present in a free state, the hydrochloric acid being 1·7 parts in 1,000, and the lactic acid in the proportion of 1 part of lactic to 9 parts of hydrochloric acid. The quantity of acid is increased by taking alcohol, and decreased by taking sugar. (*See* "Med. Examiner," Vol. i., p. 783, and Vol. ii., p. 254.)

The fact probably is, that both acids are usually present, the hydrochloric, as a rule, largely predominating over the lactic acid. In some cases, moreover, the presence of acetic, phosphoric, and butyric acids has been clearly demonstrated.

(β.) *Pepsin* is an albuminoid body, soluble in water, and insoluble in alcohol. Its solution is precipitated by corrosive sublimate, by solutions of tannic acid and of lead salts, and by alcohol. When a solution of pepsin is boiled, its action as a solvent of albuminoid matter is destroyed.

Properties, etc.—The gastric juice is a clear, acid, odorless fluid, miscible with water, and coagulating albumen. It has a specific gravity varying from 1000·1 to 1010. Its action is powerfully antiseptic. Its solution does not become turbid on boiling. It is without action on starch or on sugar when healthy. When *unhealthy*, the mucus with which it may be associated may convert cane sugar into grape sugar. It has no action on fats, but the proteid envelope of the fat is dissolved by it, whereby the fat is set free from the fat globule. Milk undergoes curdling by the action of the gastric juice; in other words, the casein is precipitated.

The action of the gastric juice as a solvent of albuminoid matters, such as fibrin, coagulated albumen, etc., depends on the joint presence of the acid and of the albuminoid ferment-body pepsin. A certain temperature (100° F.), and the perfect admixture of the fluid and food, *e.g.*, by mastication, by the muscular action of the stomach, etc., are also necessary conditions. Thus, after a time varying from two to six hours, complete chymification of the food is effected, the fibrinous and albuminous constituents being converted into different *peptones* or soluble forms of albumen, such as albumino-peptones, fibrino-peptones, gelatino-peptones, etc., all of which differ from common albumen, besides their solubility, in being uncoagulable by heat, acid, or spirit. They differ, further, from albumen in their capability of being dialysed (*albuminose* of Mialhe). The composition of the chyme depends, of course, largely on the food, but it has the general appearance of a thick fluid, and consists of a solid, undigested portion, suspended in a liquid of a more or less yellow color, and of a more or less disagreeable odor.

The Pancreatic Fluid.

This fluid, which in many respects is like the saliva (although unlike it in containing no sulphocyanide), is the secretion of the pancreas, a gland closely resembling the salivary glands.

Composition of Pancreatic Fluid per 1,000 *parts* (Schmidt).

Water	980·45		
Solids	19·55	Organic (pancreatin) ...	12·71
		Inorganic	6·84

Properties.—A colorless fluid. Specific gravity, 1008 to 1009. Its reaction is usually stated as alkaline, but this, so far as the fresh fluid is concerned, is doubtful. Its action depends on the presence of an organic principle, called *pancreatin*, an albuminoid ferment, constituting two-thirds of the total solids of the pancreatic fluid. Its action is two-fold: (1.) it emulsifies fat, converting it into a milky liquid, thereby rendering it capable of absorption by the lacteals; and (2.) it converts starch into glucose, thereby effecting its solution. (Dobell.)

The Bile.

The bile is the fluid secreted from venous blood by the cells of the liver.

Average Composition per 1,000 *parts* (Frerichs).

Water ...	859·2		
Solids ...	140·8	Biliary acids combined with alkalies (Bilin) ...	91·5
		Fat ...	9·2
		Cholesterin ...	2·6
		Mucus and coloring matters ...	29·8
		Salts ...	7·7

The quantity of solid matter is greater in the bile of the young than in that of the old. It is present in excess in such diseases as cholera, heart-disease impeding the circulation, etc., whilst it is deficient in severe inflammations, diabetes, etc.

Bile consists essentially of (1) a resinoid matter, and (2) one or more coloring bodies.

(1.) *Resinoid matter* (bilin). This consists of the soda or potash salts of two, or of one of two, acids, one of which contains sulphur and the other none—

(*a.*) Salts of *taurocholic acid* ($C_{26}H_{45}NSO_7$), which, by the action of alkalies, form *taurine* ($C_2H_7NSO_3$) together with a non-nitrogenous acid, called *cholic acid* ($C_{24}H_{40}O_5$). Thus:—

$$C_{26}H_{45}NSO_7 + H_2O = C_2H_7NSO_3 + C_{24}H_{40}O_5.$$

Taurocholic acid + Water = Taurine + Cholic acid.

Taurine may be prepared artificially by passing olefiant gas over sulphuric anhydride, neutralising the product dissolved in water with ammonia, evaporating to dryness, and heating the residue (*isethionate of ammonia*, $NH_3.H_2O.C_2H_4SO_3$), so as to expel a molecule of water.

(*β.*) Salts of *glycocholic acid* ($C_{26}H_{43}NO_6$), which, by the action of alkalies, form *glycocine* ($C_2H_5NO_2$) and *cholic acid* ($C_{24}H_{40}O_5$). Thus:—

$$C_{26}H_{43}NO_6 + H_2O = C_2H_5NO_2 + C_{24}H_{40}O_5.$$

Glycocholic acid + Water = Glycocine + Cholic acid.

[Glycocholic acid gives, on the addition of sugar and H_2SO_4, a purple red (Pettenkofer's test for bile).]

In the dog, sodium taurocholate only is present; in the pig, sodium glycocholate only is present; in man, sheep, etc., the taurocholates are in excess over the glycocholates ; whilst in the ox and in most fish, the glycocholates are in excess over the taurocholates.

Pig's bile also contains *hyocholic acid* ($C_{24}H_{40}O_4$), and goose bile *chenotaurocholic acid* ($C_{29}H_{49}NSO_6$).

(2.) The *coloring matter* of the bile is termed *cholochrome.* This is a mixture of a *green* pigment, insoluble in chloroform, called *biliverdin* ($C_{16}H_{20}N_2O_5$), and a *brown* pigment, soluble in chloroform, called *cholophæin.* Of this latter there are two modifications ; viz., the red *bilirubin* ($C_8H_9NO_2$), and the brown *biliphæin.*

A blue coloring matter has also been described.

Properties.—Bile is a viscid, greenish-yellow, bitter fluid, without odor when fresh, but very offensive after it has become putrid. It has a specific gravity of 1020. It does not readily mix with water.

Its reaction is slightly alkaline. It putrefies rapidly, becoming acid, owing to the presence of mucus derived from the gall-bladder, hepatic ducts, etc.

The action of the bile is involved in much obscurity. It does not convert starch into sugar like the saliva and pancreatic fluid (doubted by Wittich) ; it does not dissolve fibrin like the gastric juice ; it does not emulsify fat, or at any rate to the same extent, as the secretion from the pancreas. Some regard the function of the bile as the medium, by direct excretion, for the separation of an excess of carbon and hydrogen from the blood, thereby effecting its purification. This is manifestly its purpose in intra-uterine life. Nevertheless, that it is more than a mere excrementitious fluid, and plays an actual part in digestion, there can be but little doubt. Some have suggested that its function is to emulsify fat; others, that it assists the absorption of fat by moistening the intestinal mucous membrane ; others, that it neutralises the acid peptones from the stomach ; others, that its antiseptic power prevents the decomposition of the food as it passes through the bowels ; others, that it acts as a natural purgative by its stimulating effect on the intestines. As yet, however, our knowledge of the bile and its action is very imperfect.

Gall-stones consist sometimes of cholochrome held together by mucus (*oriental bezoar stones*). Most often they are formed of cholesterin around a nucleus of cholochrome. Moreover, they usually contain a certain proportion of earthy carbonates and phosphates.

The Intestinal Juice.

The fluid secreted along the whole course of the small intestines has an alkaline reaction, and contains 3 to 4 per cent. of solid matter. It has a powerful action in assisting digestion, combining the activity and digestive power of all the other secretions. Starch, fat, and albuminous substances are thus equally affected by it.

D.—EXCREMENTITIOUS PRODUCTS.

Urine; Urinary Calculi; Fæces; Sweat; Mucus; Pus.

Urine.

The urine in all animals is the vehicle through and by which the body rids itself of used-up solid matter, and of the excess of water present in the blood. It is, in short, the great outlet for the nitrogen of effete tissue.

About 60 ozs. may be taken as the average quantity of urine secreted by an adult male in 24 hours, but this is subject to great variation, depending on such causes as the quantity of fluid taken, the season of the year, and the relative activity of the skin, lungs, and alimentary canal.

Average Composition of Normal Urine, and average Quantity of the various Constituents excreted in 24 hours.

	Constituents per 1,000 parts.	Average quantity excreted in 24 hours (adult male).
Water	967·000	52·0 ozs.
Urea	14·230	512·4 grains.
Uric Acid	0·468	8·5 ,,
Extractives, Pigment, Mucus	10·167	161·0 ,,
Salts	8·135	425·0 ,,
Silica	traces.	traces.
	100·000	

(1.) The composition and character of the urine of different animals varies. Thus, in the *carnivora,* the urine is usually clear and acid, containing much urea, and but little uric acid. In the *herbivora,* it is usually turbid and alkaline, containing urea, like that of the carnivora, together with a great excess of hippuric acid, but no uric acid ; it also contains an abundance of the earthy carbonates (hence its turbidity), and but very little of the earthy phosphates, these latter being proportionately abundant in the fæces.

Carnivorous birds excrete urea in comparatively small quantity, and uric acid in abundance, *granivorous birds* excreting uric acid in abundance, but no urea. *Serpents and other land carnivorous reptiles* secrete uric acid almost entirely, whilst *frogs and other amphibious reptiles* secrete urea, and mere traces only of uric acid. Even the insecta excrete uric acid.

Thus it would seem that in the animals that drink freely, the nitrogen is excreted as urea, whilst in those that drink but little, it is excreted as uric acid. It must be noted, however, that these differences are for the most part differences of diet. For if a carnivorous animal (as a dog) be fed on a purely vegetable diet, or if a erbivorous animal (as a rabbit) be fed on a purely animal diet, a corresponding change in the composition of the urine results.

(2.) The composition of the urine varies greatly in disease. Thus he quantity of uric acid is increased in gout, etc. Albumen occurs in Bright's disease, etc.; sugar in diabetes, etc.

(3.) The composition varies hour by hour. The morning urine *urina sanguinis*) consists chiefly of the products of tissue decomposition. Hence, the choice of this by the physician for analysis. The ay and the evening urine is greatly influenced by the quantity and the character of the food ingested (*urina cibi* and *urina potûs*).

And here may be noted the changes that bodies undergo from the period of ingestion to that of urinary excretion—

(*a*.) The kidneys secrete certain bodies from the blood in an unaltered state, *e.g.*, many metals (such as As, Sb, Bi, Cu, Cr, Au, Fe, Li, Pb, Hg, Ag, Sn, Zn), free organic acids, alcohol (?), numerous salts, many of the alkaloids, such as morphia, strychnia, atropine, etc.

(*β*.) In other cases, the products secreted are oxidized products, or are otherwise changed. Thus, ammonia salts are converted into nitrates; sulphur, alkaline sulphides and sulphites, become sulphates; tannic becomes gallic acid, etc. Or, again, the neutral salts of organic acids become carbonates; free iodine is excreted as an alkaline iodide; ferrocyanides become ferricyanides; indigo blue becomes indigo white; benzoic, cinnamic, and other acids become hippuric acid, etc.

Properties.—(*a*.) *Physical.* A clear fluid of a yellow color, which, however, may vary even in health from an absence of tint to a deep orange hue. In its *specific gravity*, variations occur in health ranging from 1015 to 1025 (the average being 1020), depending on the season of the year, diet, exercise, etc. In disease the variation of specific gravity may be much greater, being sometimes as low as 1004, as in albuminuria, or as high as 1060, as in diabetes. Of its relative *clearness* it is to be noted that in health the urine often becomes turbid on cooling, due to the deposition of phosphates. The cause of its peculiar *odor* has not been well made out. The odoriferous principle, whatever it may be, undergoes speedy change.

(*β*.) *Chemical.* Healthy urine is generally acid. The acidity of the 60 oz. voided in the 24 hours may be taken as equivalent to about the acidity of 30 grains of oxalic acid. This acidity, which is least during digestion (indeed, after a meal the urine may even exhibit an alkaline reaction) and most marked during fasting, is due to the acid phosphate of sodium, and, according to some observers, to certain free acids, such as lactic acid (?).

After a certain very variable period, the urine becomes alkaline. This alkalinity is due to the urea becoming converted into carbonate of ammonia, crystals of triple phosphate, confervoid growths, and vibriones appearing simultaneously in the urine. Indeed, this change may be so rapid that under certain morbid conditions, as in cases of retention, it takes place in the bladder itself, the urine appearing turbid and alkaline when voided. The urine may, however, under certain other conditions, be alkaline when secreted. This occurs when neutral alkaline salts of the vegetable acids have been administered in excess, the acid being destroyed in the process of respiration, whilst the alkali appears in the urine as a carbonate.

We now consider in detail the various constituents of the urine :—

1. Water.—This varies according to season, exercise, drink, condition of nervous system, etc. Thus it is increased in diabetes (especially in D. insipidus), and decreased in albuminuria, in febrile affections, and in any disease increasing the secretion of water by other channels.

2. Urea.—*Carbamide* [CH_4N_2O, or $CO(NH_2)_2$], (*see* page 514).—Urea constitutes nearly one-half of the total solid matter of the urine. It is the principal outlet for the effete or excessive nitrogen of the system. The quantity excreted is greatest with an animal diet, and least with a vegetable, greater in males than in females, and greater in middle age than in youth or old age.

Constitution.—The molecular formula for urea is CH_4N_2O. It is commonly regarded as the amide of carbonic acid—that is, just as oxamide ($C_2H_4N_2O_2$) is derived from ammonic oxalate [$(NH_4)_2C_2O_4$] by the abstraction of two water molecules, so urea (CH_4N_2O) is derived from ammonic carbonate [$(NH_4)_2CO_3$].

Preparation.—(A.) *Preparation from urine.* (1.) Evaporate the urine to a syrup, and mix the concentrated liquid with an equal bulk of nitric acid. In this way a quantity of nitrate of urea will be formed ($CO(NH_2)_2HNO_3$). Dissolve this compound in boiling water, and treat the solution with barium carbonate, when pure urea remains in solution. Thus—

$$2(CO(NH_2)_2HNO_3) + BaCO_3 = CO(NH_2)_2 + Ba(NO_3)_2 + CO_2 + H_2O.$$

Nitrate of urea + Barium carbonate = Urea + Barium nitrate + Carbonic anhydride + Water.

The clear filtrate is then to be evaporated to dryness, and the urea separated from the barium nitrate by hot alcohol.

(2.) It may also be prepared by forming an oxalate of urea by the action of oxalic acid on the concentrated urine. On adding chalk to a solution of this oxalate in boiling water, calcium oxalate is precipitated, and a solution of urea formed, which may be purified by crystallization.

(B.) By the action of heat on ammonic cyanate.

(C.) By the decomposition of ammonium carbamate.

(D.) Urea was the first organic body prepared artificially, as follows: A mixture of potassium ferrocyanide (56 parts) and manganic peroxide (28 parts) is heated to redness, when the following changes occur :—

$$\begin{array}{ccccccccccc}
K_4FeCy_6 & + & O_9 & = & 4KCyO & + & 2CO_2 & + & N_2 & + & FeO \\
\text{Potassic} & + & \text{Oxygen} & = & \text{Potassic} & + & \text{Carbonic} & + & \text{Nitrogen} & + & \text{Ferrous} \\
\text{ferrocyanide} & & & & \text{cyanate} & & \text{anhydride} & & & & \text{oxide.}
\end{array}$$

The residue is now treated with cold water, and the clear filtrate containing the potassic cyanate is mixed with ammonic sulphate (41 parts). The solution is then evaporated to dryness, and the urea separated from the potassic sulphate by solution in hot alcohol :—

$$\begin{array}{ccccccc}
2KCyO & + & (NH_4)_2SO_4 & = & K_2SO_4 & + & 2CO(NH_2)_2 \\
\text{Potassic} & + & \text{Ammonic} & = & \text{Potassic} & + & \text{Urea.} \\
\text{cyanate} & & \text{sulphate} & & \text{sulphate} & &
\end{array}$$

Properties.—A colorless, inodorous body, crystallizing in long flattened prisms. It is soluble in spirit (1 in 5 at 50° F.), and very soluble in water (1 in 1 at 60° F.), the solution being neutral and permanent. Its rapid decomposition in the urine into ammonic carbonate (to which the ammoniacal odor of putrid urine is due) depends on the mucus present in the urine. When heated it melts, and finally decomposes, evolving ammonia and ammonic cyanate, and leaving a residue of cyanuric acid. It forms salts with acids, such as the nitrate of urea [$CO(NH_2)_2.HNO_3$], an important compound, an account of its difficult solubility in nitric acid. When boiled with solutions of caustic alkalies (cold solutions being without action upon it), it is resolved into ammonia and an alkaline carbonate—a similar result occurring when urea is fused with alkaline hydrates, or heated with water in a sealed tube. It combines with metallic oxides ; thus the compound $CO(NH_2)_2,2HgO$ is produced when mercuric oxide is added to a solution of urea in a potassic hydrate solution. Urea is decomposed by nitrous acid and by chlorine.

Compound ureas are formed by the replacement of the hydrogen of the urea by hydrocarbon groups. In *sulpho-urea,* sulphur takes the place of oxygen [$CS(NH_2)_2$].

3. Uric Acid; *Lithic Acid* ($C_5N_4H_4O_3$).—This is present in the urine in combination with soda and ammonia, and is probably derived from the disintegrated elements of albuminous tissues. The salts of uric acid, being more soluble in warm than in cold water, are frequently deposited as the urine cools. This specially results in certain deranged states of the constitution, where an excess of uric acid is present.

The quantity of uric acid in human urine is increased by an animal diet and decreased by a vegetable diet. It is increased in certain diseased conditions. It varies greatly in different animals. In the feline tribe, uric acid is often entirely replaced by urea. In birds and serpents, the urea is often entirely replaced by uric acid. This suggests the notion that although urea and uric acid may have a different origin and different offices, nevertheless that the one may do the work of the other.

Urate of soda constitutes the chief constituent of the gouty concretions known as "*chalk-stones.*"

Preparation.—A. *From urine.*—By adding HCl to the concentrated urine. The uric acid is precipitated in the form of hard red grains.

B.—*From the excrement of serpents.*—This consists mainly of an acid ammonium urate. Dissolve the excrement in a boiling solution of potassic hydrate ; filter, and add hydrochloric acid to the filtrate, when the uric acid is precipitated as a white crystalline powder. "Guano" is an impure uric acid, formed by the partial decomposition of the excrement of sea birds.

Properties.—Uric acid is a tasteless, inodorous, and sparingly soluble body (1 in 10,000). It is insoluble in alcohol or in ether, but is soluble in strong sulphuric acid. When heated in a retort, a black residue remains, cyanic acid, hydrocyanic acid, carbonic anhydride, and ammonium carbonate being evolved.

Uric acid is a dibasic acid. Fused with an alkaline hydrate, it yields an alkaline carbonate, cyanate and cyanide. Mixed with nitric acid, it effervesces. If the resulting acid solution be evaporated nearly to dryness, and after dilution be mixed with a slight excess of ammonia, the characteristic deep red tint of *murexide* ($C_8N_6H_8O_6$) is immediately produced.

With hydriodic acid and heat, uric acid is resolved into glycocin, carbonic anhydride, and ammonia.

Some Products of the Oxidation of Uric Acid.

Name.	Formulæ.	Preparation and Properties.
Allantoïn	$C_4N_4H_6O_3$	*Preparation.*—(1.) From the allantoic fluid of fœtal calf. (2.) By boiling uric acid with water and peroxide of lead. *Properties.*—Transparent colorless crystals ; soluble in 160 parts of cold water. Decomposed by boiling with mineral acids and caustic alkalies.
Alloxan ..	$C_4N_2H_2O_4 4aq$	*Preparation.*—By the action of strong nitric acid on uric acid in the cold. *Properties.*—White crystals ; very soluble in water ; crystals become anhydrous at 150° C. Solution acid, and stains the skin red. Decomposed by both oxidizing and reducing agents. Forms a deep blue compound when acted on with an alkali and a ferrous salt. Alloxan appears to be the intermediate stage in the conversion, by oxidation, of uric acid into urea. When alloxan is boiled with peroxide of lead, urea is formed— $(C_4N_2H_2O_4+2PbO_2+H_2O=CH_4N_2O+3CO_2+2PbO)$. Alloxan forms *alloxantin* by the action of sulphuretted hydrogen.
Alloxantin	$C_8N_4H_4O_7 3aq$	*Preparation.*—(1.) By the action of hot dilute nitric acid on uric acid. (2.) By the action of reducing agents (as H_2S) on alloxan. *Properties.*—Colorless crystals. Soluble with difficulty in cold water, more soluble in hot. Becomes anhydrous at 150° C. Solution acid. Gives a violet precipitate with baryta water, and a black precipitate with $AgNO_3$—Converted by oxidizing agents into alloxan. Boiled in water with peroxide of lead, it forms urea and plumbic carbonate. Decomposed by the prolonged action of H_2S into dialuric acid.

Name.	Formulæ.	Preparation and Properties.
Alloxanic acid	$C_4N_2H_4O_5$	*Preparation.*—By the action of baryta water on a solution of alloxan. The Ba is to be separated by H_2SO_4. *Properties.*—A crystalline bibasic acid. The solution is acid, and decomposes carbonates. It dissolves Zn with the disengagement of hydrogen. The silver alloxanate is insoluble. On boiling in water alloxanic acid forms urea and mesoxalic acid ($C_3O_3(OH)_2$).
Mesoxalic acid	$C_3O_3(OH)_2$	*Preparation.*—(1.) By heating a solution of baric alloxanate to boiling. (2.) By adding a solution of alloxan to lead acetate, and decomposing the lead mesoxalate with H_2S. Urea is formed at the same time. *Properties.*—A crystalline acid. It resists heat. The silver mesoxalate is insoluble.
Parabanic acid	$C_3N_2H_2O_3$	*Preparation.*—By the action of moderately strong nitric acid on uric acid or on alloxan, with the aid of heat. *Properties.*—A crystalline acid. The solution neutralised with ammonia and boiled, yields an ammonium salt of oxaluric acid.
Thionuric acid	$C_4N_3H_5SO_6$	*Preparation.*—By the action of a sulphurous acid solution on a cold solution of alloxan, and afterwards boiling the mixture with ammonia and ammonic carbonate. The ammonic thionurate formed is to be converted into a lead salt, which is then decomposed with sulphuretted hydrogen. *Properties.*—By boiling the solution it is resolved into sulphuric acid and uramil.
Uramil ..	$C_4N_3H_5O_3$	*Preparation.*—By boiling a solution of ammonic thionurate with a slight excess of hydrochloric acid. *Properties.*—A white crystalline body. Its ammoniacal solution turns purple in air. It is decomposed into alloxan and ammonic nitrate by nitric acid.
Murexide (Purpurate of ammonia)	$C_8N_6H_8O_6+aq$	*Preparation.*—(1.) By heating dry alloxantin with ammonia. (2.) By boiling uramil and mercuric oxide in a weak solution of ammonia. *Properties.*—The crystals appear green by reflected, and purple red by transmitted light. It is insoluble in alcohol and ether. It is soluble in hot, but not very soluble in cold water. It is decomposed by mineral acids, a white body (murexan) being precipitated. It is soluble in KHO, the solution being purple red, and disappearing on boiling.
Dialuric acid	$C_4N_2H_4O_4$	*Preparation.*—By the long continued action of H_2S on a boiling solution of alloxan. It is the final product of the action of reducing agents on alloxan.
Oxaluric acid	$C_3N_2H_4O_4$	

4. Hippuric Acid ($C_9H_9NO_3$) ; *Benzamidacetic acid* ($C_2H_3[NH(C_7H_5O)]O_2$) ; *Benzoyl glycocoll* ($C_2H_4(C_7H_5O)NO_2$).—This acid is found in large quantities in the urine of herbivorous animals, but it also occurs in small quantities in the urine of man. It is derived partly from certain constituents of vegetable diet, and partly from the natural disintegration of tissue.

The relationship between hippuric acid and benzoic acid should be noted. The urine of a cow or horse at rest yields, by the action of hydrochloric acid, hippuric acid ; but if the animals are being actively worked, their urine yields benzoic acid, and not hippuric acid. Moreover, the *fresh urine only* yields hippuric acid, the same urine when stale yielding benzoic acid. If benzoic acid be administered to an animal, hippuric acid is found in the urine.

The urine of children is said sometimes to contain benzoic acid.

Preparation.—(1.) Evaporate cows' urine to a thick syrup, and add to the concentrated urine an excess of hydrochloric acid. Hippuric acid will be deposited on standing.

(2.) By the action of benzoyl chloride on zinc glycocoll :—

$$\underset{\text{Zinc glycocoll}}{Zn''(C_2H_4NO_2)_2} + \underset{\substack{\text{Benzoyl}\\\text{chloride}}}{2C_7H_5OCl} = \underset{\substack{\text{Zincic}\\\text{chloride}}}{ZnCl_2} + \underset{\substack{\text{Hippuric}\\\text{acid.}}}{2C_9H_9NO_3.}$$

Properties.—Rhombic prisms soluble in hot alcohol and in cold water (1 in 400). Solution acid. Forms crystallizable salts. The acid is monobasic. When heated it yields benzoic acid, benzoate of ammonia and benzonitrile, a black residue remaining in the vessel. It is converted into benzoic acid by sulphuric acid, and into benzoic acid and glycocine ($C_2H_5NO_2$) by hydrochloric acid. Nitrous acid converts it into benzoglycollic acid ($C_9H_8O_4$) which by the action of boiling water is converted into benzoic ($C_7H_6O_2$) and glycollic acids ($C_2H_4O_3$).

It is to be remarked that hippuric acid is soluble in an aqueous solution of sodic phosphate, which probably explains the acid reaction of the urine.

5. Salts.—These consist essentially of sulphuric, phosphoric, and hydrochloric acids combined with soda, potash, lime, and magnesia. The ash also contains a trace of iron.

The quantity of saline matter in normal urine varies between 8 and 9 grains per 1,000 grains of urine, but the quantity is largely influenced by diet (an animal diet increasing the quantity of sulphates), mental energy, etc.

6. Extractive Matter.—This includes kreatin, kreatinin (derived from the metamorphosis of muscular tissue), xanthin, and other bodies, such as indican, glucose, etc.

7. Pigments.—The pigments of the urine are not well understood. They are probably altered hæmoglobin. A body called *urohæmatin* has been mentioned by Harley, and one called *urochrome* by Thudichum. Other pigments variously named purpurin, rosacic acid, and uroerythrin have also been described.

Schunck considers that the urinary pigments described are products of two colouring matters always present in urine, the one being soluble in ether, having the composition $C_{43}H_{51}NO_{26}$, and the other insoluble in ether, having the composition $C_{19}H_{27}NO_{14}$.

In jaundice the urine is colored by bile pigment.

8. Free Gases.—It was found that 100 c.c. of urine yielded at normal temperature and pressure the following gases :—

Nitrogen	0·87
Oxygen	0·06
Carbonic anhydride, *free*	4·54
„ „ *combined*	2·07

It is to be noted that the composition of the urine is largely influenced by disease. Thus albumen appears in Bright's disease, glucose in diabetes, etc.

Urinary Calculi.

A few general analytical remarks are all that is necessary here.

On heating a very small piece of the calculus on platinum foil, one of two results may occur :—

A. *It may be entirely, or very nearly entirely, dissipated.*

[*Conclusion.*—It is probably uric acid; but it may be urate of ammonia, cystine, or xanthin.]

Calculus.	Physical Characters.	Action of Water, Alkalies, etc.	Action of Acids, etc.
Uric acid, $C_5N_4H_4O_3$.	Brownish red; smooth or tuberculated; concentric laminæ (common).	Insol. in water; sol. by heat in solution of KHO, without the generation of ammonia. A ppt. of uric acid occurs when an acid is added to the alkaline solution.	Dissolves with effervescence in HNO_3. The residue on evaporation is *red*, becoming purple red on the addition of ammonia (=purple red murexide).
Urate of ammonia.	Clay colored; smooth; fine concentric laminæ (rare).	Sol. in water; sol. by heat in solution of KHO, ammonia fumes being evolved.	
Cystine $C_3H_7NSO_2$).	Brownish yellow: semi-transparent; crystalline (very rare).	Insol. in water, in alcohol, or in ether; sol. in ammonia, when the solution is evaporated spontaneously, it leaves hexagonal plates. The ammonia solution is precipitated by an acid.	Odor of CS_2 when heated. Sol. in a solution of KHO. If acetate of lead be added to a boiling solution, a black ppt. of PbS results.
Xanthin ($C_5H_4N_4O_2$).	Pale brown; polished appearance (very rare).	Sol. in alkaline solutions.	Sol. in HNO_3 *without* effervescence. Residue on evaporation, a *deep yellow* color. Sol. in boiling HCl.

B. *It may not be dissipated by heat.*

[*Conclusion.*—It is probably oxalate of lime or fusible calculus, but it may be phosphate of lime or ammonio-phosphate of magnesia.]

Calculus.	Physical Characters.	Action of Ammonia on Acid Solutions.	Action of Acids, Blow pipe, etc.
Oxalate of lime (mulberry calculus).	Deep brown; rough; very hard; layers thick (common).	The solution in HCl gives a white amorphous ppt. with ammonia.	Sol. in HCl without effervescence; insol. in acetic acid. When heated it becomes $CaCO_3$, when it dissolves in HCl with effervescence, but on being heated more strongly CaO only remains, which is alkaline to turmeric.
Phosphate of lime (bone earth calculus).	Pale brown color; laminæ regular (rare).	The solution in HCl gives a white amorphous gelatinous ppt. with ammonia.	Sol. in HCl; insol. in acetic acid. Infusible before the blow pipe. The residue on being strongly heated is not alkaline.
Ammonio-phosphate of magnesia (triple phosphate).	White, brittle, and crystalline; surface uneven; seldom laminated (rare).	The solution in acids gives a white crystalline ppt. with ammonia.	Sol. in HCl and in acetic acid. Fusible before blow-pipe with difficulty, evolving NH_3. Residue insol. in water and not alkaline.
Mixed phosphate of lime and ammonio-phosphate of magnesia (fusible calculus).	White; often very large; fusible and rarely laminated (common).	The solution in HCl or acetic acid gives a white ppt. with ammonia (phosphate of magnesia) and a white ppt. with oxalate of ammonia (lime).	Sol. in acetic acid; insol. in KHO. Very fusible by blow pipe, residue being insol. in water, but sol. in acids. Residue not alkaline.

Fæces.

These constitute the excrementitious portions of food. The chemical composition of the solid matter of the excrement varies with the food taken. The fæces consist (on an average) of about 25 per cent. of solid matter, the rest being water. The solid portion is made up of biliary matter, alimentary débris, and salts, these latter being mainly phosphates of lime and magnesia, with small quantities of iron, soda, lime, and silica. The offensive odor of fæcal matter is due to certain intermediate products of oxidation, and becomes more offensive as the quantity of bile that is secreted diminishes.

Excretin ($C_{78}H_{156}SO_2$), a body melting at 204·8° F. (96° C.), soluble in water and hot alcohol, and insoluble in cold alcohol, has been discovered by Marcet in the alcoholic extract of fæcal matter.

Excretolic acid (Marcet) consists of a mixture of fatty acids, precipitated by the action of lime on an alcoholic extract of fæcal matter.

Sweat. Mucus. Pus.

Sweat is the watery excretion from the sudoriparous glands of the skin. Its reaction is usually acid, from the presence of free lactic and formic acids, etc. It contains from 0·5 to 2·00 per cent. of solid matter, the quantity varying with the temperature of the day, the liquids taken, the amount of exercise, etc. The chief part of the solid matter consists of sodium chloride, but traces of phosphate of lime, together with lactates, butyrates, and acetates are also present. A trace of urea is said to be constant. A peculiar azotized and easily decomposed body and an odorous principle are present in varying quantity. Carbonic acid and nitrogen are also given off by the skin.

Mucus is a viscid matter secreted by the mucous membranes. It is always, more or less largely, mixed with epithelium cells. Its glairy consistence is due to the presence of a nitrogenized body called *mucin*, the percentage composition of which is said to be carbon 52·2, hydrogen 7·0, nitrogen 12·6, and oxygen 28·2.

Mucin swells up when subjected to the action of water, but it is not soluble in water. It is turned yellow by nitric acid. It is not precipitated by mercuric chloride, acetic acid, plumbic acetate, or potassic ferrocyanide. It is coagulated by alcohol and by heat.

Pus is a creamy-white fluid, having a neutral or slightly alkaline reaction. It appears under the microscope to consist of minute globules floating in a transparent serum. The pus globules are only imperfectly dissolved by alkalies. They contain fat (2 to 6 per cent.) and cholesterin (1 per cent.). Dilute acids distend them. The serum of pus contains albumin, leucin, and an albuminoid body called "*pyin*."

Pyin is soluble in water. It is precipitated by acetic acid. Unlike mucin, it is precipitated both by mercuric chloride and by lead acetate.

Cholesterin, $C_{26}H_{43}OH$, is a fat-like body, soluble in ether, in boiling alcohol, and in chloroform. It is the chief constituent of biliary calculi.

The solid residue of pus contains 12 per cent. of saline matter, phosphoric acid and potash being the principal acid and base present.

APPENDIX.

TABLE I.

Table showing the Specific Gravities and percentage strengths of various solutions of Nitric Anhydride (N_2O_5) *and Nitric Acid* (HNO_3).

Specific Gravity.	HNO_3=63.	N_2O_5=108.	Specific Gravity.	HNO_3=63.	N_2O_5=108.
1·5000	92·983	79·700	1·2947	46·299	39·685
1·4980	92·053	78·903	1·2887	45·562	39·053
1·4960	91·124	78·106	1·2826	44·632	38·256
1·4940	90·194	77·309	1·2765	43·702	37·459
1·4910	89·264	76·512	1·2705	42·772	36·662
1·4880	88·334	75·715	1·2644	41·842	35·865
1·4850	87·404	74·918	1·2583	40·913	35·068
1·4820	86·484	74·121	1·2523	39·983	34·271
1·4790	85·545	73·324	1·2462	39·053	33·474
1·4760	84·615	72·527	1·2402	38·123	32·677
1·4730	83·680	71·730	1·2341	37·190	31·880
1·4700	82·755	70·933	1·2277	36·263	31·083
1·4670	81·825	70·136	1·2212	35·334	30·286
1·4640	80·895	69·339	1·2148	34·404	30·489
1·4600	79·966	68·542	1·2084	33·474	28·692
1·4570	79·036	67·745	1·2019	32·544	27·895
1·4530	78·106	66·948	1·1958	31·614	27·098
1·4500	77·181	66·155	1·1895	30·684	26·301
1·4460	76·246	65·354	1·1833	29·755	25·504
1·4424	75·316	64·557	1·1770	28·825	24·707
1·4385	74·386	63·760	1·1709	27·890	23·910
1·4346	73·457	62·963	1·1648	26·965	23·113
1·4336	72·527	62·166	1·1587	26 035	22·316
1·4269	71·587	61·396	1·1526	25·105	21·519
1·4228	70·667	60·572	1·1465	24·176	20·722
1·42 B.P.	70·000	60·000	1·1403	23·246	19·925
1·4189	69·737	59·775	1·1345	22·316	19·128
1·4147	68·807	58·978	1·1286	21·386	18·331
1·4107	67·878	58·181	1·1227	20·456	17·534
1·4065	66·948	57·384	1·1168	19·526	16·737
1·4023	66·018	56·587	1·1109	18·597	15·940
1·3978	65·090	55·790	1·1051	17·667	15·143
1·3945	64·158	54·993	1·1010	17·442	14·950
1·3882	63·229	54·196	1·0993	16·737	14·346
1·3833	62·299	53·399	1·0935	15·807	13·549
1·3783	61·369	52·602	1·0878	14·877	12·752
1·3732	60·439	51·805	1·0821	13·947	11·955
1·3681	59·579	51·068	1·0764	13·017	11·158
1·3630	58·579	50·211	1·0708	12·088	10·361
1·3579	57·650	49·414	1·0651	11·158	9·564
1·3529	56·720	48·617	1·0595	10·228	8·767
1·3477	55·790	47·820	1·0540	9·298	7·970
1·3427	54·860	47·023	1·0485	8·368	7·173
1·3376	53·930	46·226	1·0430	7·439	6·376
1·3323	53·000	45·429	1·0375	6·508	5·579
1·3270	52·069	44·632	1·0320	5·579	4·782
1·3216	51·141	43·835	1·0267	4·649	3·985
1·3163	50·211	43·038	1·0212	3·719	3·188
1·3110	49·281	42·241	1·0159	2·789	2·391
1·3056	48·355	41·447	1·0106	1·860	1·594
1·3001	47·180	40·440	1·0053	0·930	0·797

Table II.

Showing the Percentage of real Sulphuric Acid (H_2SO_4) *corresponding to various Specific Gravities of Aqueous Sulphuric Acid.*

Bineau; Otto. Temp. 15°

Specific Gravity.	Per cent. of H_2SO_4.	Specific Gravity.	Per cent. of H_2SO_4.	Specific Gravity.	Per cent. of H_2SO_4.	Specific Gravity.	Per cent. of H_2SO_4.
1·8426	100	1·675	75	1·398	50	1·182	25
1·842	99	1·663	74	1·3886	49	1·174	24
1·8406	98	1·651	73	1·379	48	1·167	23
1·840	97	1·639	72	1·370	47	1·159	22
1·8384	96	1·627	71	1·361	46	1·1516	21
1·8376	95	1·615	70	1·351	45	1·144	20
1·8356	94	1·604	69	1·342	44	1·136	19
1·834	93	1·592	68	1·333	43	1·129	18
1·831	92	1·580	67	1·324	42	1·121	17
1·827	91	1·568	66	1·315	41	1·1136	16
1·822	90	1·557	65	1·306	40	1·106	15
1·816	89	1·545	64	1·2976	39	1·098	14
1·809	88	1·534	63	1·289	38	1·091	13
1·802	87	1·523	62	1·281	37	1·083	12
1·794	86	1·512	61	1·272	36	1·0756	11
1·786	85	1·501	60	1·264	35	1·068	10
1·777	84	1·490	59	1·256	34	1·061	9
1·767	83	1·480	58	1·2476	33	1·0536	8
1·756	82	1·469	57	1·239	32	1·0464	7
1·745	81	1·4586	56	1·231	31	1·039	6
1·734	80	1·448	55	1·223	30	1·032	5
1·722	79	1·438	54	1·215	29	1·0256	4
1·710	78	1·428	53	1·2066	28	1·019	3
1·698	77	1·418	52	1·198	27	1·013	2
1·686	76	1·408	51	1·190	26	1·0064	1

TABLE III.

Table showing the percentage quantities of Hydrochloric Acid, Sp. Gr. 1·2, and of Hydrochloric Acid Gas contained in Aqueous Solutions of different Specific Gravities.

Specific Gravity.	Acid of Sp. Gr. 1·2.	Hydrochloric Acid Gas.	Specific Gravity.	Acid of Sp. Gr. 1·2.	Hydrochloric Acid Gas.
1·2000	100	40 777	1·0980	49	19·980
1·1982	99	40·369	1·0960	48	19·572
1·1964	98	39·961	1·0939	47	19·165
1·1946	97	39·554	1·0919	46	18·757
1·1928	96	39·146	1·0899	45	18·349
1·1910	95	38·738	1·0879	44	17·941
1·1893	94	38·330	1·0859	43	17·534
1·1875	93	37·923	1·0838	42	17·126
1·1857	92	37·516	1·0818	41	16·718
1·1846	91	37·108	1·0798	40	16·310
1·1822	90	36·700	1·0778	39	15·902
1·1802	89	36·292	1·0758	38	15·494
1·1782	88	35·884	1·0738	37	15·087
1·1762	87	35·476	1·0718	36	14·679
1·1741	86	35·068	1·0697	35	14·271
1·1721	85	34·660	1·0677	34	13·863
1·1701	84	34·252	1·0657	33	13·094
1·1681	83	33·845	1·0637	32	12·597
1·1661	82	33·437	1·0617	31	12·300
1·1641	81	33·029	1·0597	30	11·903
1·1620	80	32·621	1·0577	29	11·506
1·1599	79	32·213	1·0557	28	11·109
1·1578 B.P.	78	31·805	1·0537	27	10·712
1·1557	77	31·398	1·0517	26	10·316
1·1536	76	30·990	1·0527	B. P.	10·290
1·1515	75	30·582	1·0497	25	0·919
1·1494	74	30·174	1·0477	24	9·922
1·1473	73	29·767	1·0457	23	9·126
1·1452	72	29·359	1·0437	22	8·729
1·1431	71	28·951	1·0417	21	8·332
1·1410	70	28·544	1·0397	20	7·935
1·1389	69	28·136	1·0377	19	7·538
1·1369	68	27·728	1.0357	18	7·141
1·1349	67	27·321	1·0337	17	6·745
1·1328	66	26·913	1·0318	16	6·348
1·1308	65	26 508	1·0388	15	5·951
1·1287	64	26·098	1·0279	14	5·544
1·1267	63	25·690	1·0259	13	5·158
1·1247	62	25·282	2·0239	12	4·762
1·1226	61	24·874	1·0220	11	4·365
1·1206	60	24·466	1·0200	10	3·998
1·1185	59	24·058	1·0180	9	3·571
1·1164	58	23·650	1·0160	8	3·174
1·1143	57	23·242	1·0140	7	2·778
1·1123	56	22·834	1·0120	6	2·381
1·1102	55	22·426	1·0110	5	1·984
1·1082	54	22·019	1·0080	4	1·588
1·1061	53	21·611	1·0060	3	1·191
1·1041	52	21·203	1·0040	2	0·795
1·1020	51	20·796	1·0020	1	0·397
1·1000	50	20·388			

TABLE IV.

Showing the Percentage Amount of Ammonia (NH_3) *in Aqueous Solutions of the Gas of various Spccific Gravities.*

Carius. Temp. 14°.

Specific Gravity.	NH_3 per cent.	Specific Gravity.	NH_3 per cent.	Specific Gravity.	NH_3 per cent.
0·8844	36	0·9133	24	0·9520	12
0·8864	35	0·9162	23	0·9556	11
0·8885	34	0·9191	22	0·9593	10
0·8907	33	0·9221	21	0·9631	9
0·8929	32	0·9251	20	0·9670	8
0·8953	31	0·9283	19	0·9709	7
0·8976	30	0·9314	18	0·9749	6
0·9001	29	0·9347	17	0·9790	5
0·9026	28	0·9380	16	0·9831	4
0·9052	27	0·9414	15	0·9873	3
0·9078	26	0·9449	14	0·9915	2
0·9106	25	0·9484	13	0·9959	1

TABLE V.

Showing the Percentage Amount of Potash (K_2O) *in Aqueous Solutions of various Specific Gravities.*

Tünnermann, N. Tr. xviii., 2, 5. Temp. 15°.

Specific Gravity.	Per Cent. of K_2O.	Specific Gravity.	Per Cent. of K_2O.
1·3300	28·290	1·1437	14·145
1·3131	27·158	1·1308	13·013
1·2966	26·027	1·1182	11·882
1·2805	24·895	1·1059	10·750
1·2648	23·764	1·0938	9·619
1·2493	22·632	1·0819	8·487
1·2342	21·500	1·0703	7·355
1·2268	20·935	1·0589	6·224
1·2122	19·803	1·0478	5·002
1·1979	18·671	1·0369	3·961
1·1839	17·540	1·0260	2·829
1·1702	16·408	1·0153	1·697
1·1568	15·277	1·0050	0·5658

TABLE VI.

Showing Percentage Amount of Soda (Na_2O) *in Aqueous Solutions of various Specific Gravities.*

Tünnermann.

Specific Gravity.	Per cent. of Na_2O.	Specific Gravity.	Per cent. of Na_2O.	Specific Gravity.	Per cent. of Na_2O.	Specific Gravity.	Per cent. of Na_2O.
1·4285	30·220	1·3198	22·363	1·2392	15·110	1·1042	7·253
1·4193	29·616	1·3143	21·894	1·2280	14·500	1·0948	6·648
1·4101	29·011	1·3125	21·758	1·2178	13·901	1·0855	6·044
1·4011	28·407	1·3053	21·154	1·2058	13·297	1·0764	5·440
1·3923	27·802	1·2982	20·550	1·1948	12·692	1·0675	4·835
1·3836	27·200	1·2912	19·945	1·1841	12·088	1·0587	4·231
1·3751	26·594	1·2843	19·341	1·1734	11·484	1·0500	3·626
1·3668	25·989	1·2775	18·730	1·1630	10·879	1·0414	3·022
1·3586	25·385	1·2708	18·132	1·1528	10·275	1·0330	2·418
1·3505	24·780	1·2642	17·528	1·1428	9·670	1·0246	1·813
1·3426	24·176	1·2578	16·923	1·1330	9·066	1·0163	1·209
1·3349	23·572	1·2515	16·379	1·1233	8·462	1·0081	0·604
1·3273	22·967	1·2453	15·714	1·1137	7·857	1·0040	0·302

TABLE VII.

Proportion of Absolute Alcohol by Weight in 100 *parts of Spirit, of different Specific Gravities at* 60° F.

(Fownes. *Phil. Trans.*, 1847.)

Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.
0·5	1·0000	25	·9652	51	·9160	76	·8581
0	0·9991	26	·9638	52	·9135	77	·8557
1	0·9981	27	·9623	53	·9113	78	·8533
2	0·9965	28	·9609	54	·9090	79	·8508
3	0·9947	29	·9593	55	·9069	80	·8483
4	0·9930	30	·9578	56	·9047	81	·8459
5	0·9914	31	·9560	57	·9025	82	·8434
6	0·9898	32	·9544	58	·9001	83	·8408
7	0·9884	33	·9528	59	·8979	84	·8382
8	0·9869	34	·9511	60	·8956	85	·8357
9	0·9855	35	.9490	61	·8932	86	·8331
10	0·9841	36	·9470	62	·8908	87	·8305
11	0·9828	37	·9452	63	·8886	88	·8279
12	0·9815	38	·9434	64	·8863	89	·8254
13	0·9802	39	·9416	65	·8840	90	·8228
14	0·9789	40	·9396	66	·8816	91	·8199
15	0·9778	41	·9376	67	·8793	92	·8172
16	0·9766	42	·9356	68	·8769	93	·8145
17	0·9753	43	·9335	69	·8745	94	·8118
18	0·9741	44	·9314	70	·8721	95	·8089
19	0·9728	45	·9292	71	·8696	96	·8061
20	0·9716	46	·9270	72	·8672	97	·8031
21	0·9704	47	·9249	73	·8649	98	·8001
22	0·9691	48	·9228	74	·8625	99	·7969
23	0·9678	49	·9206	75	·8603	100	·7938
24	0·9665	50	·9184				

In this Table every alternate number is the result of a direct synthetical experiment; absolute alcohol and distilled water being weighed out in the proper proportions, and mixed by agitation in stoppered bottles; after a lapse of three or four days, each specimen was brought exactly to 60° F. and the specific gravity determined with great care.

TABLE VIII.

Specific Gravities corresponding to Degrees of Baumé's Hydrometer for Liquids heavier than Water. (Water = 1·000.)

Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.
0	1·000	20	1·152	40	1·357	60	1·652
1	1·007	21	1·160	41	1·369	61	1·670
2	1·013	22	1·169	42	1·382	62	1·689
3	1·020	23	1·178	43	1·395	63	1·708
4	1·027	24	1·188	44	1·407	64	1·727
5	1·034	25	1·197	45	1.420	65	1·747
6	1·041	26	1·206	46	1·434	66	1·767
7	1·048	27	1·216	47	1·448	67	1·788
8	1·056	28	1·225	48	1·462	68	1·809
9	1·063	29	1·235	49	1·476	69	1·831
10	1·070	30	1·245	50	1·490	70	1·854
11	1·078	31	1·256	51	1·495	71	1·877
12	1·085	32	1·267	52	1·520	72	1·900
13	1·094	33	1·277	53	1·535	73	1·924
14	1·101	34	1·288	54	1·551	74	1·949
15	1·109	35	1·299	55	1·567	75	1·974
16	1·118	36	1·310	56	1·583	76	2·000
17	1·126	37	1·321	57	1·600		
18	1·134	38	1·333	58	1·617		
19	1·143	39	1·345	59	1·634		

Specific Gravities on Baumé's Scale for Liquids lighter than Water.

Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.
10	1·000	23	0·918	36	0·849	49	0·789
11	0·993	24	0·913	37	0·844	50	0·785
12	0·986	25	0·907	38	0·839	51	0·781
13	0·980	26	0·901	39	0·834	52	0·777
14	0·973	27	0·896	40	0·830	53	0·773
15	0·967	28	0·890	41	0·825	54	0·768
16	0·960	29	0·885	42	0·820	55	0·764
17	0·954	30	0·880	43	0·816	56	0·760
18	0·948	31	0·874	44	0·811	57	0·757
19	0·942	32	0·869	45	0·807	58	0·753
20	0·936	33	0·864	46	0·802	59	0·749
21	0·930	34	0·859	47	0·798	60	0·745
22	0·924	35	0·854	48	0·794		

Table IX.

Degrees on Twaddell's Hydrometer, and the corresponding Specific Gravities.

[Note.—The degrees of Twaddell's hydrometer are converted into their corresponding specific gravities by multiplying by 0·005, and adding 1·000. Conversely, to convert specific gravity into degrees Twaddell, deduct 1,000 and divide the remainder by 5. Thus:—

25 Twaddell × 5 + 1000 = 1125 specific gravity.
1125 specific gravity — 1000 ÷ 5 = 25 Twaddell.]

Degrees Twaddell.	Specific Gravity.	Degrees Twaddell.	Specific Gravity.	Degrees Twaddell.	Specific Gravity.
1	1·005	8	1·040	15	1·075
2	1·010	9	1·045	16	1·080
3	1·015	10	1·050	17	1·085
4	1·020	11	1·055	18	1·090
5	1·025	12	1·060	19	1·095
6	1·030	13	1·065	20	1·100
7	1·035	14	1·070		

Table X.

English Weights and Measures.—Avoirdupois.

	Grs.	Drms.	Ozs.	lbs.	Qrs.	Cwt.	Tons.
Grain	1						
Drachm ..	27·34	1					
Ounce	437·5	16	1				
Pound	7000	256	16	1			
Quarter ..	196000	7168	448	28	1		
Cwt.	784000	28672	1792	112	4	1	
Ton	15680000	573440	35840	2240	80	20	1

Troy Weight.

	Grains.	Dwts.	Ounces.	lb.
Grain	1			
Pennyweight	24	1		
Ounce	480	20	1	
Pound	5760	240	12	1

1 cubic inch of distilled water in air at 62° F. = 252·456 grains.
1 cubic inch of distilled water *in vacuo* at 62° F. = 252·722 grains.

	Cubic inches.
1 gallon	= 277·276 (100 c.i. = 0·3606 gallon).
1 pint	= 34·659
1 fluid ounce	= 1·7329
1 litre	= 61·024
1 cubic centimètre	= 0·061024

1 cubic inch = 16·387 cubic centimètres.

(*For comparison of French and English weights, see page* 62.)

	Cubic inches.	Litres.
1 gallon	277·276	4·54345797
1 pint	34·659	0·567932

A cubic inch of water weighs	252·45	grains.
,, ,, ,, ,, hydrogen ,,	0·0214	,,
,, ,, ,, ,, oxygen ,,	0·3428	,,
,, ,, ,, ,, mercury ,,	3425·25	,,

A pint (imperial) of water (= 34·65 C.I.) weighs 1·25 lbs.
A gallon ,, ,, ,, (= 277·274 C·I.) ,, 10·0 lbs.

A hundred weight (1 cwt.) of water measures 11·2 gallons or 1·8 cubic feet.
A ton of water measures 224 gallons or 35·84 cubic feet.
100 C. I. of water = 0·3606 gallon.

TABLE XI.

To Reduce Grammes to Grains.

Log. Grammes + 1·188432 = log. grains.

To Reduce Cubic Centimètres to Cubic Inches.

Log. cubic centimètres + (—2·7855007) = log. cubic inches.

To Reduce Millimètres to Inches.

Log. millimètres + (—2·5951663) = log. inches.

To Convert Grains into Grammes.

Log. grains + (—2·8115680) = log. grammes.

To Convert Cubic Inches into Cubic Centimètres.

Log. cubic inches + 1·2144993 = log. cubic centimètres.

To Convert Inches into Millimètres.

Log. inches + 1·4048337 = log. millimètres.

TABLE XII.

Table of the corresponding Heights of the Barometer in Millimètres and English Inches.

Milli-mètres.	=	English inches.	Milli-mètres.	=	English inches.	Milli-mètres.	=	English inches.
720	=	28·347	739	=	29·095	758	=	29·843
721	=	28·386	740	=	29·134	759	=	29·882
722	=	28·425	741	=	29·174	760	=	29·922
723	=	28·465	742	=	29·213	761	=	29·961
724	=	28·504	743	=	29·252	762	=	30·000
725	=	28·543	744	=	29·292	763	=	30·039
726	=	28·583	745	=	29·331	764	=	30·079
727	=	28·622	746	=	29·370	765	=	30·118
728	=	28·662	747	=	29·410	766	=	30·158
729	=	28·701	748	=	29·449	767	=	30·197
730	=	28·740	749	=	29·488	768	=	30·236
731	=	28·780	750	=	29·528	769	=	30·276
732	=	28·819	751	=	29·567	770	=	30·315
733	=	28·858	752	=	29·606	771	=	30·355
734	=	28·898	753	=	29·645	772	=	30·394
735	=	28·937	754	=	29·685	773	=	30·433
736	=	28·976	755	=	29·724	774	=	30·473
737	=	29·016	756	=	29·764	775	=	30·512
738	=	29·055	757	=	29·803			

TABLE XIII.

For Converting Degrees of the Centigrade Thermometer into Degrees of Fahrenheit's Scale.

Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.
—90°	—130°	—60°	—76°	—30°	—22°
85	121	55	67	25	13
80	112	50	58	20	4
75	103	45	49	15	+ 5
70	94	40	40	10	14
65	85	35	31	5	23
0°	+32°	+100°	+212°	+200°	+392°
+ 5	41	105	221	205	401
10	50	110	230	210	410
15	59	115	239	215	419
20	68	120	248	220	428
25	77	125	257	225	437
30	86	130	266	230	446
35	95	135	275	235	455
40	104	140	284	240	464
45	113	145	293	245	473
50	122	150	302	250	482
55	131	155	311	255	491
60	140	160	320	260	500
65	149	165	329	265	509
70	158	170	338	270	518
75	167	175	347	275	527
80	176	180	356	280	536
85	185	185	365	285	545
90	194	190	374	290	554
95	203	195	383	295	563

1° F. = 0·55° C.
2 = 1·11
3 = 1·66
4 = 2·22
5 = 2·77

1° C. = 1·8° F.
2 = 3·6
3 = 5·4
4 = 7·2
5 = 9

To Convert F. into C. degrees and C. into F. degrees.

$$\frac{(\text{F.}^\circ - 32) \times 5}{9} = \text{C.}^\circ\text{; or } (\text{F.}^\circ - 32) \div 1{\cdot}8 = \text{C.}^\circ.$$

$$\frac{\text{C.}^\circ \times 9}{5} + 32 = \text{F.}^\circ\text{; or } (\text{C.}^\circ \times 1{\cdot}8) + 32 = \text{F.}^\circ.$$

To convert F. into Reaumur and Reaumur into F.

$$\frac{(\text{F.} - 32) \times 4}{9} = \text{R.} \qquad \frac{\text{R} \times 9}{4} + 32 = \text{F.}$$

To convert C. into Reaumur and Reaumur into C.

$$\frac{\text{C} \times 4}{5} = \text{R.} \qquad \frac{\text{R} \times 5}{4} = \text{C.}$$

TABLE XIV.

Table of the Tension of Aqueous Vapor expressed in Inches of Mercury, at 32° F., for each degree F. between 0° and 100°.

Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.
0	0·0439	26	0·1395	51	0·3742	76	0·8964
1	0·0459	27	0·1457	52	0·3882	77	0·9266
2	0·0481	28	0·1522	53	0·4026	78	0·9577
3	0·0503	29	0·1589	54	0·4175	79	0·9898
4	0·0526	30	0·1660	55	0·4329	80	1·0227
5	0·0551	31	0·1733	56	0·4488	81	1·0566
6	0·0576	32	0·1810	57	0·4653	82	1·0915
7	0·0603	33	0·1883	58	0·4822	83	1·1274
8	0·0630	34	0·1959	59	0·4997	84	1·1643
9	0·0659	35	0·2038	60	0·5178	85	1·2023
10	0·0689	36	0·2119	61	0·5364	86	1·2413
11	0·0721	37	0·2204	62	0·5556	87	1·2815
12	0·0753	38	0·2291	63	0·5755	88	1·3228
13	0·0788	39	0·2381	64	0·5959	89	1·3652
14	0·0823	40	0·2475	65	0·6170	90	1·4088
15	0·0861	41	0·2571	66	0·6388	91	1·4537
16	0·0899	42	0·2672	67	0·6612	92	1·4998
17	0·0940	43	0·2775	68	0·6843	93	1·5471
18	0·0982	44	0·2882	69	0·7081	94	1·5958
19	0·1027	45	0·2993	70	0·7327	95	1·6657
20	0·1073	46	0·3108	71	0·7580	96	1·6971
21	0·1121	47	0·3226	72	0·7841	97	1·7498
22	0·1171	48	0·3349	73	0·8109	98	1·8039
23	0·1223	49	0·3476	74	0·8386	99	1·8595
24	0·1278	50	0·3607	75	0·8671	100	1·9170
25	0·1335						

This Table is computed from Regnault's experiments, and is taken from Dixon's "Treatise on Heat," p. 257.

TABLE XV.

Table showing the number of Gallons and Cubic Feet of Water over various Areas at various Depths from 0·25 inch to 1 Foot.

Depth.	Cubic Feet on				Gallons on			
	One Square Foot.	One Square Yard.	One Acre.	One Square Mile.	One Square Foot.	One Square Yard.	One Acre.	One Square Mile.
1 foot 0 inches ..	1	9	43,560	27,878,400	6·23	56·07	271,378	173,682,432
,, 11 ,, ..	0·92	8·25	39,930	25,555,200	5·70	51·38	248,764	159,208,896
,, 10 ,, ..	0·83	7·50	36,300	23,232,000	5·18	46·71	226,150	144,735,360
,, 9 ,, ..	0·75	6·75	32,670	20,908,800	4·66	42·01	203,533	130,261,824
,, 8 ,, ..	0·66	6·00	29,040	18,585,600	4·16	37·36	180,920	115,788,288
,, 7 ,, ..	0·58	5 25	25,410	16,262,400	3·63	32·70	158,301	101,314,752
,, 6 ,, ..	0·50	4·50	21,780	13,939,200	3·11	28·03	135,689	86,841,216
,, 5 ,, ..	0·42	3·75	18,150	11,616,000	2·59	23·35	113,075	72,367,680
,, 4 ,, ..	0·33	3·00	14,520	9,292,800	2·08	18·68	90,460	57,894,144
,, 3 ,, ..	0·25	2·25	10,890	6,969,600	1·55	14·01	67,844	43,420,608
,, 2 ,, ..	0·17	1·50	7,260	4,646,400	1·04	9·34	45,230	28,947,072
,, 1 ,, ..	0·08	0·75	3,630	2,323,200	0·52	4·67	22,615	14,473,536
,, 0¾ ,, ..	0·06	0·56	2,722	1,742,400	0·39	3·49	16,960	10,855,152
,, 0½ ,, ..	0·04	0·37	1,815	1,161,600	0·26	2·33	11,307	7,236,768
,, 0¼ ,, ..	0·02	0·18	907	580,800	0·13	1·16	5,653	3,618,384

INDEX.

A.

PAGE
"A" and "ia," the terminations . 29
Abnormal vapor densities . . . 45
Absolute contact 2
Absorption of gases 7, 10, 241
Absorption, coefficient of . . 231, 241
Acenaphthene 642
Acetal 746
Acetaldehyde 745
Acetamide 695, 703, 759
Acetates 702
  reactions of the 727
Acetenylbenzene 640
Acetic chloride 703
  ether 703
  peroxide 703
  series, acids of the 697
  —aldehydes of the 744
Acetification of alcohol 586, 590, 701
Acetone 666, 748, 749
Acetonitril 762
Acetous fermentation . . . 580, 586
Acetyl 693
Acetyl chloride 695, 703
Acetylene 273, 274, 592, 630, 633, 638
  synonyms, preparation, properties, 274
  test 275
  series, preparation, properties . 633
Acid albumen 796
Acid, definition of 291, 293
Acid, abietic 653
  acetic, 579, 586, 592, 666, 696, 698, 701
  —reactions 727
  —metallic salts of 702
  —derivatives of 703
  —action of chlorine on . . 696, 703
  —ketone of 748
  —fermentation 586
  acrylic 696, 711, 717, 746
  adipic 718
  alloxanic 829
  alphatoluic 713
  alphaxylic 713
  amido-acetic 703, 802
  amido-benzoic 715
  amido-caproic 705, 802
  amylhydro-oxalic 707
  anchoic 718
  angelic 711
  anisic 715
  anthracene carboxylic . . 696, 717
  anthraquinone-disulphonic . . 645
  antimonious 489, 491
  antimonic 489, 491

PAGE
Acid—*continued.*
  arachidic 698
  arsenic 496, 500
  arsenious 496, 498
  arsenmethylic 764
  atropic 717
  auric 507
  behenic 698
  benzamidacetic 714, 829
  benzoic 636, 637, 642, 670, 696, 712, 713, 717, 721, 726
  —reactions 729
  bisulphuretted hyposulphuric . 190
  boric (boracic) 219
  brassic 711
  bromic 105
  bromobenzoic 714
  bromocinnamic 717
  bromopropionic 599
  bromosuccinic 599
  butylactic 707
  butyric, 580, 666, 698, 704, 720, 726, 771
  —fermentation 580
  camphoric 652
  capric 698
  caproic 580, 698, 705
  caprylic 698
  carbamic 708
  carbocresylic 715
  carbohydroquinonic 716
  carbolic 592, 596, 657, 670
  carbonic 210, 214, 707, 708
  —absorption of by carbon . . . 204
  —estimation of in air 125
  —preparation, properties, etc., of 211
  carminic 785
  cerebric 803
  cerotic 698
  chenotaurocholic 823
  chlorhydric 250
  chloric 96, 100
  chlorobenzoic 714
  chlorocarbonic 216
  chlorochromic . . . 316, 412, 417
  chlorosulphuric 178
  chlorous 96, 99
  chlorocrotonic 712
  chloropropionic 709
  chlorovaleric 705
  cholic 823
  chromic 412, 414
  —a powerful oxidizing agent . 603

PAGE

Acid—*continued.*
chromous . . . 413
chrysammic . . . 784
cimicic . . . 711
cinnamic . . . 696, 717, 747
citraconic . . . 724
citric . . . 725
—reactions . . . 728
coumaric . . . 715
cresotic . . . 715
cresylic . . . 592
crotonic . . . 711
cumic . . . 713
cyanic . . . 610
cyanuric . . . 610, 611
damaluric . . . 711
damolic . . . 711
dephlogisticated marine . . . 88
desoxalic . . . 725
diacetotartaric . . . 723
dialuric . . . 829
diamyloxalic . . . 707
dibromacetic . . . 696, 703
dichloracetic . . . 696, 703
dichlor - anthracene - disulphonic . . . 645
diethacetic . . . 704
dinitrososulphonic . . . 133
dimethacetic . . . 697
diphosphoric . . . 162
dioxyacetic . . . 710
dioxybenzoic . . . 716
dioxypropionic . . . 710
dioxysuccinic . . . 722
disulpho-dithionic . . . 190
dithionic . . . 176
dithionous . . . 176, 188, 189
doeglic . . . 711
elaidic . . . 711, 736
erucic . . . 711, 733
ethacetic . . . 704
ethyloxalic . . . 720
ethylsulphuric . . . 274
ethylenelactic . . . 709
ethylic . . . 701
excretolic . . . 832
ferric . . . 407
ferricyanic . . . 616
— reactions of . . . 730
ferrocyanic . . . 614
— reactions of . . . 730
fluoboric . . . 221
formic, 666, 683, 698, 700, 709, 723, 726
formobenzoic . . . 715
fulminic . . . 610, 612
fulminuric . . . 610, 611
fumaric . . . 274, 599, 696, 724
gaidic . . . 711
gallic . . . 696, 716
— reactions . . . 730
gallotannic . . . 736
glyceric . . . 677, 696, 709, 710
glycocholic . . . 822
glycollic . . . 674, 707, 708, 741

PAGE

Acid—*continued.*
glyoxalic . . . 709, 747
glyoxylic . . . 710
Graham's sulphuric . . . 183
graphic, or graphitic . . . 199, 203
gummic . . . 689
heptylic . . . 705
hexylic . . . 705
hippuric . . . 714, 727, 829
— reactions . . . 728
hyænasic . . . 698
hydriodic . . . 178, 255
— action on organic bodies . . . 599
hydrobromic . . . 253
hydrochloric . . . 250
— table showing the percentage quantities of, in aqueous solutions of different specific gravities . . . 837
— absorption by carbon . . . 204
—solution of, preparation, properties, impurities . . . 250-253
hydrocinnamic . . . 717
hydrocyanic . . . 605, 726, 749
— Scheele's test for . . . 618
— reactions of . . . 619
hydrocoumaric . . . 715
hydrofluoboric . . . 221
hydrofluoric . . . 256
hydrofluosilicic . . . 226, 257, 336
hydromellonic . . . 612
hydro-nitroprussic . . . 617
hydroparacoumaric . . . 715
hydroselenic . . . 270
hydro-sulphocyanic . . . 217
hydrosulphuric . . . 266
— action of, on the metals . . . 288
hydrosulphurous . . . 189
hyocholic . . . 823
hypobromous . . . 104
hypochloric . . . 99
hypochlorous . . . 96, 97, 387
— as a bleaching agent . . . 98
hypogæic . . . 711
hyponitric (nitric peroxide) . . . 134
hyponitrous . . . 128, 130, 133
hypophosphoric . . . 158
hypophosphorous . . . 158, 159
hyposulphuric (dithionic acid) . 189
hyposulphurous . . . 189
— (thiosulphuric acid) . . . 188
iodacetic . . . 703
iodic . . . 110
iodopropionic . . . 710
isatropic . . . 717
isophthalic . . . 724
isobutyric . . . 697, 704
isopropylacetic . . . 705
isoamylic . . . 705
isosuccinic . . . 721
itaconic . . . 724
kakodylic . . . 765
lactic . . . 579, 696, 707, 708
—fermentation . . . 579
lauric . . . 698

PAGE
Acid—*continued.*
leucic 707
lithic 827
maleic 724
malic 696, 718, 720, 721, 723, 728
malonic 718, 722
mandelic 715
manganic 392, 395
mannitic 678
margaric 698, 706
marine 250
meconic 725
—reactions of 730
melissic 698
mellitic 725
mesaconic 724
mesitic 697
mesoxalic 722, 829
metabismuthic 465, 466
metabismuthous 465, 466
metaboric 219
metagallic 716
metagummic 689
metantimonic 491, 493
metantimonious 491
metaphosphoric 158, 161, 165
metarsenic 500
metastannic 491
metatoluic 634
metatungstic 554
metavanadic 504
methacetic 697, 704
methacrylic 711
methethacetic 705
methylcrotonic 711
methylic 700
metoxybenzoic 715
molybdic 516
monobromacetic 696, 703
monochloracetic 696, 703
mono-oxy-acetic 708
moringic 711
moritannic 784
muriatic (*see* Hydrochloric).
mucic 679, 688
myristic 698
myronic 686
naphthalene-sulphonic 641
naphthalic 642
naphthoic 696, 717
nitric 140
—action of, on metals 143
—commercial preparation of 141
—impurities of 142
—preparation of 141
—preparation of pure acid 142
—properties of 142
—reactions of 144
—synonyms, history 140
—table showing the specific gravities and percentage strengths of 835
—chloride of 148
—fuming 142
nitrobenzoic 714

PAGE
Acid—*continued.*
nitro-hydrochloric 143
nitrous 134
—preparation and properties of 134
—(nitrous anhydride) 133
—(nitric peroxide) 134
—action of, on the metals 287
nonylic 698
Nordhausen sulphuric 181
octylic 698
œnanthylic 698, 705
oleic 698, 711, 718
ortharsenic 500
orthoboric 219
orthophosphoric 158, 163, 165
orthoxybenzoic 715
osmic 475
oxalic 599, 677, 718, 719
—commercial preparation of 719
—reactions 727
oxaluric 829
oxybenzoic 715
oxybutyric 707
oxycaproic 707
oxycholic 672
oxygenated muriatic 88
oxymalonic 720
oxymethylbenzoic 715
oxymuriatic 88, 100
oxypicric 784
oxysalicylic 696, 716
oxysuccinic 721
oxytricarballylic 725
oxyvaleric 707
palmitic 698, 705
palmitolic 712
parabanic 829
paralactic 709
paramalic 708
paraoxybenzoic 715
pectic 793
pectonic 793
pelargonic 698
pentathionic 176, 191
pentylic 704
perbromic 105
perchloric 96, 101
perchromic 250, 412, 419
periodic 110
permanganic 392, 395
pernitrous 133
persulpho-molybdic 517
phenic 670, 726
phenylbenzoic 646
phenylic 670
phenyl-lactic 715
phenyl-propiolic 696, 717
phlogisticated vitriolic 176
phloretic 715
phospho-molybdic 317, 516
phosphoric 158, 163, 602
—hexabasic 158
—glacial 161
—monobasic 161
—tribasic 163

PAGE

Acid—*continued.*
  phosphoric reactions of . . . 165
  —action on organic bodies of . 600
  phosphorous 158, 160
  phthalic 636, 641, 696, 724
  picric 671, 784
  pimelic 718
  pinic 653
  piperic 716
  platinic 512
  plumbic 525
  propionic . . 697, 698, 704, 709, 711
  propylic 704
  prussic 605
  pyrantimonic 491
  pyrarsenic 500
  pyrocatechuic 716
  pyrogallic 677, 716
  pyrophosphoric . . .158, 162, 165
  pyroracemic 709
  pyrosulphuric 183
  pyrotartaric 718
  pyroterebic 711
  pyrovanadic 504
  propyl-acetic 704
  pyruvic 696, 709
  quinic 716
  racemic 709, 723
  ricinoleic 733
  rocellic 718
  ruberythric 687, 785
  ruthenic 477
  rutic 698
  saccharic 678
  salicylic 696, 715
  sarcolactic 709
  sebacic 718
  selenhydric 270
  selenic 196
  selenious 194, 195
  separgylic 718
  silicic 223, 226, 336
  silico-fluoric 257
  silico-formic, or leukon . . . 226
  silico-tungstic 555
  sorbic 696, 712
  stannic 481
  stearic 698, 706
  stearolic 712
  suberic 718
  succinic 579, 654, 695, 696, 718, 720, 723, 726
  —reactions 721, 729
  sulpharsenic 501
  sulpharsenious 496, 501
  sulphbenzoic 598
  sulphantimonic 496
  sulphantimonious 494
  sulphhydric 266
  sulphidic 266
  sulphocarbonic 216, 217
  sulphocyanic 612
  —reactions 730
  sulphodithionic 190
  sulphoethylic (*see* Sulphovinic).

PAGE

Acid—*continued.*
  sulphoglyceric 598, 676, 735
  sulphokakodylic 765
  sulphomolybdic 517
  sulpho-sulphuric 188
  sulphovinic 273, 598, 739
  sulphovinylic 667
  sulphuretted hyposulphuric . . 190
  sulphuric 176, 181
  —Nordhausen 409
  —action on organic bodies . . 598
  —nitrous 182
  —table showing the percentage of real, corresponding to various specific gravities of aqueous sulphuric acid 836
  sulphurous 176, 179
  —and sulphuric acids in the air 126
  tannic 716
  —reactions 730
  tartaric . . 6, 60, 96, 718, 709, 722
  —reactions 729
  tartronic 721, 722, 723
  taurocholic 823
  telluric 197
  tellurous 197
  terephthalic 637, 646, 724
  tetraboric 219
  tetrathionic 176, 190
  tetroleic 712
  tetrylic 704
  thiacetic 703
  thiocyanic 612
  thionuric 829
  thiosulphuric 176, 188
  —distinguished from sulphurous acid 189
  thymotic 715
  thymylcarbonic 715
  titanic 485
  toluic 713
  tribromacetic 703
  tricarballylic 697, 725
  trichloracetic . . . 696, 703, 745
  trimethacetic 697
  trioxybenzoic 716
  trioxycarballylic 725
  trisulphodithionic 191
  trisulphuretted hyposulphuric . 191
  trithionic 176, 190
  tungstic 554
  ulmic 682
  uric 727, 827, 831
  —reactions 728
  —products of oxidation . . . 828
  valerianic 704
  valeric 667, 698, 704
  valero-lactic 707
  vanadic 504
  vitriolic 181
  xanthic 708
  xylic 713
  xylilic 713

PAGE
Acids . . . 293
  action of heat on . . . 5
  action of, on salts in solution . 8
  as disinfectants . . . 588
  of different basicities . . . 293
  water unites with the anhydrides to form . . . 28
  types of different . . . 293
  reactions of some of the chief organic . . . 726
  organic . . . 692
  —classification of the . . . 696
  —substitution derivatives of the 696
  —haloid salts of the . . . 695
  —salts of . . . 693
  —chlorides, bromides, etc., of . 695
  —amides of . . . 695
  —compound ethers of . . . 694
  —constitution of the . . . 693
  —derivatives of . . . 693
  —relationships of . . . 693
  —anhydrides or oxides of . . . 694
  —peroxides of . . . 694
  —acetic series of . . 696, 697, 710
  —acrylic series of . . . 696, 710
  —benzoic series of . . . 696, 712
  —biliary . . . 823
  —cinnamic series of . . . 696, 716
  —dibasic . . . 718
  —fatty series of . . . 698
  —formation from alcohols . . 697
  —fumaric series of . . . 696, 724
  —gallic series of . . . 696, 716
  —glyoxylic series of . . . 696, 710
  —isoxybenzoic series of . 696, 716
  —lactic series of . . . 696, 706
  —malic series of . . . 696, 721
  —mesitic series of . . . 696
  —monobasic . . . 697
  —naphtoic series of . . . 696, 717
  —olefine series of (primary, secondary, and tertiary) . . 706
  —oxybenzoic series of . . 696, 714
  —phthalic series of . . . 696, 724
  —primary, secondary, and tertiary of acetic series of . . 697
  —pyruvic series of . . . 696, 709
  —salicylic series of . . . 714
  —sorbic series of . . . 696, 712
  —succinic series of . . . 696, 718
  —tartaric series . . . 696, 722
  —tricarballylic series of . 696, 725
  sulphonic . . . 679
Acidum phosphoricum dilutum (B.P.) . . . 163
Aconitine . . . 774
  tests for . . . 781
Acrolein . . . 600, 676, 732, 746
  series, acids of the . . . 696, 710
  —aldehydes of the . . . 744, 745
Adamant . . . 199
Adhesion, affinity measured by the force of . . . 22
  attraction between dissimilar molecules . . . 1

PAGE
Adhesion—*continued.*
  modifies chemical action . . . 7
Æsculin . . . 686
Æthiop's mineral . . . 547
Affinity (chemical) . . . 1
  definition, 1; conditions necessary for the exertion of affinity, 2; phenomena of affinity, 2; changes in the sensible properties, 3; in the physiological properties, 3; in the physical properties, 3; circumstances influencing affinity, 4-21; gravitation, 4; cohesion, 4; elasticity, 5; adhesion, 7; influence of mass or quantity on affinity, 11; mechanical force may modify chemical action, 12; contact decomposition, 12; influence of heat and cold, 14; influence of light, 18; influence of electricity, 18; influence of vitality, 20; degree, force, or energy of affinity, 21; affinity measured by reference to the specific gravity of bodies, 21; by the force of adhesion, 20; by the amount of force required to effect the decomposition of a compound, 22; by the time of combination, 24; by combining proportions, 24; by the electrical condition, 26
After damp . . . 211
Agate, amorphous variety of silica . . . 223
Aggregation . . . 3
Aich metal . . . 456
Air, oxygen and nitrogen in . . . 120
  ammonia in . . . 126
  carbonic acid in . . . 124
  moisture in . . . 123
  nitric acid in . . . 127
  organic matter in . . . 127
  ozone in . . . 122
  sulphurous acid in . . . 127
Air, weight of the . . . 118
  specific gravity of the . . . 118
  pressure of the . . . 119
  average temperature of the . . 119
  warmth of, due to radiation . . 119
  a refractor of light . . . 119
  a mechanical mixture . . . 119
  analysis of . . . 120
  alkaline . . . 259
  atmospheric . . . 118
  —history . . . 118
  —properties . . . 118
  —composition . . . 120
  dephlogisticated . . . 68
  empyreal . . . 68
  fixed or mephitic . . . 210
  hepatic . . . 266
  inflammable . . . 227
  —heavy . . . 271

PAGE
Air—*continued.*
  pure 68
  vital 68
  moisture in 124
  pure and impure 126
Alabaster 379, 383
Albite 338, 443
Albumen, acid 796
  alkaline 796
Albumen in blood 814
Albumens 795
  derived 796
Albuminates 796
Albuminoids or proteids 794
  reactions of the 798
Albuminose 821
Alcohol 663
  allylic 667
  amylic 657, 667
  benzylic 669, 670
  butylic 626, 657, 666, 704
  caproic 657
  caprylic 657
  cetylic 657
  cinnamic 657, 672
  cresylic 669, 672
  cumilic 669
  decatylic 657
  dimethyl phenylic 669
  ethylic 657, 663
  —preparation from elements of 661
  —reactions of 690
  heptylic 657
  hexylic 657
  lauric 657
  melissic 657
  methylic 657, 662
  —preparation of 659
  nonylic 657
  octylic 657
  œnanthic 657
  pentylic 657
  phenylic 669, 670
  propargylic 657, 668
  propenyl 675
  propylic 657, 665, 693
  rutic 657
  sycocerylic 669
  thymylic 669, 672
  toluylic 669
  vinylic 657, 667
  xylilic 669
Alcohol, proportion of absolute, by weight in 100 parts of spirit of different specific gravities at 60° F. 839
  reactions of 690
  an, what it is 656
  acetification of 586, 590, 700
  action of chlorine on 93
Alcohol dehydrogenatum (aldehyde) 743
Alcoholates 664
Alcoholic or vinous fermentation 579

PAGE
Alcohols, The 656
  division of, into primary, secondary and tertiary 658
  relation of, to the organic acids 697
  —to the haloid ethers 656
  —to the oxy-ethers 656
  —to the compound ethers 656
  reactions of the 690
  cyanides of the 762
  dihydric 672
  aldehydes of the 747
  ethers of the 740
  ethylic series 657
  vinylic series 657
  benzylic series 657
  cinnamic series 657
  glyceric series 657
  pyrogallic series 657, 677
  $C_nH_{2n-3}(OH)$ series 657, 668
  $C_nH_{2n-5}(OH)$ series 657, 675
  preparation of normal primary 659
  products of oxidation of primary 659
  — —secondary 659
  — —tertiary 659
  saligenin series 674
  hexhydric 678
  mercaptans or thio- 679
  monohydric 657
  —ethers of 738
  tetrahydric 657
  trihydric 657
  —ethers of 741
  supplementary chapter to the 680
Aldehyde 745
  acetic 744, 745
  acrylic 746
  alpha-toluic 746
  ammonium 745
  anisic 746
  benzoic 670, 686, 717, 746
  butyric 744
  caproic 744
  cinnamic 747
  crotonic 746
  cumic 746
  cuprylic 744
  ethylic 745
  formic 744, 745
  glycolic 674
  green 759
  isobutyric 744
  isovaleric 744
  methylic 745
  œnanthylic 744
  oxalic 747
  palmitic 744
  paratoluic 746
  propionic 744, 748
  resin of 745
  salicylic 675, 746
  sycocerylic 746
  valeric 744

PAGE
Aldehydes, The . . . 743
  distinction from ketones . . . 749
  of the acetic series . . . 744
  of the acrylic series . . . 746
  of the benzoic series . . . 746
  of the dihydric alcohols . . . 747
  of series ($C_nH_{2n-9}COH$) . . . 747
Aldol . . . 745
Algaroth, powder of . . . 493
Alizarin . . . 644, 783, 785
Alkalamide . . . 760
Alkali albumen . . . 796
Alkali, volatile . . . 259
Alkali waste . . . 172, 188, 358
  works, red liquor of . . . 354, 358
Alkalies, action of, on organic bodies . . . 600
  metals of the . . . 288
  as disinfectants . . . 589
  organic — the natural alkaloids . . . 768
  —definition, history, natural history; preparation, properties; action of heat, of light, of electricity, of solvents, of acids, of alkalies, of the haloids, of metallic salts, of nascent oxygen on the . . . 768-770
Alkaline air . . . 259
  carbonates, action of, on organic matter . . . 600
  earths, metals of the . . . 374
  hydrates, action of the fixed, on organic bodies . . . 600
  metals . . . 339
  waters . . . 246
Alkaloids . . . 750
  natural . . . 768
  volatile . . . 768
  tests for certain of the . . . 780
  of vegetable origin . . . 760
  —extraction of, from plants . . . 772
  of animal origin . . . 776
  —reaction of the . . . 780
  constitution of the . . . 777
Alkarsin . . . 764
Allantoin . . . 828
Allotropism . . . 61
Alloxan . . . 602, 828
Alloxantin . . . 828
Alloys . . . 289
  changes in the sensible and physical properties of . . . 290
  changes in the chemical properties of . . . 291
Allylamine . . . 753
Allylbenzene . . . 640
Allylene . . . 633
Allylpyridine . . . 771
Almonds, artificial oil of . . . 639
Alum works, liquor of . . . 389, 441
Alums, the . . . 440
Alum (potassic aluminic sulphate), 438, 440
Alum, flour . . . 441

PAGE
Alum—*continued.*
  meal . . . 441
  silver . . . 442
  cæsium . . . 442
  thallium . . . 442
  indium . . . 435
  ammonia . . . 438
  soda . . . 438
  selenium . . . 440
  cake . . . 440
  chrome . . . 412, 417, 440, 442
  common . . . 441
  concentrated . . . 440
  gallium . . . 447
  iron . . . 405, 410, 441
  manganese . . . 398, 442
  —aluminium . . . 398
  potash . . . 438, 440
  Roman . . . 442
  shale . . . 441
  burnt . . . 442
Alumina . . . 438
Aluminates . . . 439
Aluminium . . . 437
  history, natural history, preparation, properties . . . 437-438
  compounds of . . . 438
  bronze . . . 438, 456
  reactions of the salts of . . . 446
Aluminium acetate . . . 702
  bromide . . . 438
  calcic silicate . . . 335
  chloride . . . 438, 439, 589
  colloidal . . . 439
  fluoride . . . 438, 440
  hydrate . . . 439
  iodide . . . 438, 440
  manganous sulphate . . . 442
  methide . . . 757
  nitrate . . . 438
  oxide . . . 438
  phosphate . . . 150, 438, 442
  potassic sulphate . . . 438, 441
  silicate . . . 335, 437, 438, 440
  sulphate . . . 438, 440
  sulphide . . . 438, 440
Amalgamation, process for extraction of silver . . . 530
Amalgams . . . 289, 539
Amarine . . . 755
Amber . . . 653, 654
American ash . . . 348
Amethyst, crystalline variety of silicia . . . 222
Amides . . . 733, 759
  acid . . . 259
  of monatomic acids . . . 760
  of diatomic and triatomic acids . 761
  primary, secondary and tertiary . . . 760
  constitution of . . . 760
Amido-benzene . . . 755
Amidogen . . . 258, 259
Amido-paraffins . . . 629
Amido-toluene . . . 754

PAGE

- Amine, ethyl phenyl 756
  - diethyl phenyl 756
  - phenyl 755
- Amines, The 629, 750
- Amines, primary, secondary, and tertiary 750
- Ammonia 258, 259, 368
  - synonyms, history, natural history, preparation, 259; properties, 260.
  - table showing the percentage amount of, in aqueous solutions of the gas of various specific gravities 838
  - absorption by carbon of . . . 204
  - in air 126
  - in iron rust 259
  - in rain water 126
  - from coal 592
  - bases produced by the action of, on the chlorides of platinum . 513
  - carbonate of 371
  - hydrosulphate of 370
  - impurities of 262
  - molecule of 42
  - soda process, for preparing carbonate of soda 359
  - solution of 262, 368
- Ammonides, The 367
- Ammonio-phosphate of magnesia 390
- Ammonium 258, 262, 376
  - acetate 702
  - aldehyde 745
  - amalgam 262, 367
  - bicarbonate 368, 371
  - borate 336
  - bromate 368
  - bromide 368, 369
  - carbonates 368, 371, 592
  - chlorate 325, 368
  - chloride 368, 369
  - —abnormal vapor density of 45, 369
  - chromate 412
  - compounds with platinum . . 513
  - cyanate 607, 610
  - cyanide 592, 607
  - dichromate 412
  - dithionate 320, 368
  - ferrous sulphate 409
  - fluoride 368, 369
  - heptasulphide 368, 370
  - hydrate 368
  - hydric sulphate 368, 371
  - hydric sulphide 368, 370
  - hydrosulphate 370
  - iodate 368
  - iodide 368, 369
  - iridic chloride 518
  - magnesic phosphate . . . 388, 390
  - molybdate 317
  - nitrate 368, 371
  - nitrite 324, 368, 372
  - oxalate 604, 720
  - pentasulphide 370

PAGE

- Ammonium—*continued.*
  - perchlorate 368
  - permanganate 396
  - phosphate 164, 372
  - phosphomolybdate 516
  - platinic chloride 368, 511
  - platinum chloride 369
  - protosulphide 369
  - purpurate 829
  - pyrophosphate 368
  - pyrosulphite 368
  - reactions of compounds of . . 372
  - silico fluoride 368
  - sesquicarbonate 368, 371
  - sodium phosphate 368, 372
  - sodium sulphate 368, 371
  - sulphate 367, 368, 370
  - sulphhydrate 368, 370
  - sulphides . . . 368, 369, 370, 592
  - sulphite 368
  - sulphocyanide 592, 612
  - sulphamate 180
  - tartrates 723
  - thiosulphate 368
  - urate 831
  - vanadate 504
- Ampère, law of 38
- Amygdalin 686
- Amylamine 753
- Amylbenzene 637
- Amylene 630
- Amylglycerin 675
- Amylic acetate 703, 742
- Amyloid (proteid) 798
- Amyloses, The 687
- Analysis and synthesis 27
- Analysis, organic 560
- Analcime 443
- Anatase 484
- Anethene 651
- Anglesite 520, 529
- Angostura bark 774
- Anhydride, definition of 28
  - acetic 703
  - antimonic 491
  - antimonious 490
  - arsenic 500
  - arsenious 498
  - auric 506, 507
  - benzoic 714
  - bismuthic 465, 466
  - boric 219
  - carbonic 210
  - —decomposition of, by plants . 85
  - chlorous, non-existence of . . . 96
  - chromic 412, 414
  - hypochlorous 96
  - hyponitrous 128
  - iridic 518
  - iodic 110
  - lactic 709
  - manganic 392, 395
  - molybdic 515
  - nitric 139
  - —specific gravities and percent-

PAGE

Anhydride—*continued.*
age strengths of various solutions of 838
—synonyms, preparation and properties 133
nitrous 132, 133
osmic 475
permanganic 392, 395
persulphuric 176, 187
phosphoric 161
phosphorous 160
ruthenic 477
selenious 195
silicic 222
stannic 481
sulphantimonic 494
sulphantimonious 494
sulphuric 176, 180
sulpharsenic 501
sulpharsenious 501
sulphurous 176
tartaric 723
telluric 197
tellurous 197
titanic 486
tungstic 554
uranic 432
vanadic 504
Anhydrides, The 244
Anhydrite 383
Aniline 592, 639, 753
origin of name, synonyms; constitution, 755; properties, uses, 756.
tests for 11
dyes 757, 758
Animal charcoal 801
Animal chemistry 794
Animal fluids, nutrient 803
solids 799
manganese in 391
Annatto 784
Anorthite 335, 338
Anthracene 592, 596, 643, 717
preparation, properties 643
series 642
Anthracite, or steam coal . 198, 205, 206
Anthrachrysone 716
Anthraquinone 644
Antichlor 95, 179, 318, 319
Antimonates, The. 333, 491
Antimonites, The 491, 494
Antimonic chloride 489, 493
chlorosulphide 493
fluoride 489
oxide 489
—hydrates (acids) of 489
oxy-chloride 489, 493
sulphide 489, 494
sulpho-trichloride 493
Antimonious antimoniate . . . 489
anhydride 490
argentide 489
bromide 489
chloride 489, 492

PAGE

Antimonious—*continued.*
fluoride 489
hydride 311, 489
iodide 489
oxide 489, 490, 491
oxychloride 489, 493
sulphide 489, 493
Antimoniuretted or antimonetted hydrogen 489
Antimonoso-antimonic oxide . . 491
Antimony 487
history, natural history, preparation, properties, uses . . 487, 488
compounds of 489
reaction of the salts of 494
amalgam 492
amorphous 488
butter of 492
chlorosulphide of 493
crude 171
crystalline 488
glass of 494
grey ore of 488
ochre 488
pentachloride of 493
pentasulphide of 494
regulus of 488
sesquioxide of 490
terchloride of 492
tersulphide or sesquisulphide of . 493
vermilion 493
Antiseptic, an, what it is 588
Ants, acid present in 700
Antozone 80
Apatite 87, 150, 379, 385
Apocodeine 769
Apomorphia 769
Aqua fortis (nitric acid) 140
Aqua lauro-cerasi 605
Aquamarine 447
Aqua regia 143
Aquates 244
Aqueous vapor, determination of in air 123
table of the tension of, expressed in inches of mercury 845
opacity to heat 240
power of carbon for absorbing . 203
Arabin 580, 689
Archil and Cudbear, preparation of 783
Argentic arsenate 332
acetate 702
arsenite 333, 499
bromate 532
bromide 532, 535
carbonate 532
chlorate 328, 532
chromate 412
chloride 532, 534
cyanide 532, 607
cyanurate 608
dichromate 412
dithionate 320
fluoride 532, 535

PAGE
Argentic—*continued.*
  fulminate 608, 612
  hydrate 368
  hyposulphite 532
  iodate 532
  iodide 532, 535
  mellonide 612
  metaphosphate 532
  nitrate 532, 536
  nitrite 532
  orthophosphate 532
  oxide 532, 533
  periodate 327
  permanganate 396
  peroxide 532, 533
  phosphate 532
  phosphide 532
  pyrophosphate 532
  selenite 196
  sulphantimonite 334, 494, 530
  sulpharsenite 334, 532
  sulphate 532, 536
  sulphide 532, 536
  sulphite 532
  thiosulphate 318, 532
Argentite 536
Argentous oxide 532, 533
  chloride 532, 534
Argentum vivum 538
Argol 722
Aricin 772, 773
Arnicin 653
Aromatic series, The 634
Aromatic plants, action of 77
Arragonite 384
Arsen-dimethyl 764
Arsen-monomethyl 764
Arsenates, The 331, 500
Arsenic 498
  reactions of the compounds 501
Arsenic acid 496, 500
  anhydride 496, 500
  compounds of 496
  sulphide 496, 501
  terchloride of 502
  tersulphide of 501
  trihydride of 497
  white 498
  trioxide 498
"Arsenic bloom" 498
Arsenical iron 501
  nickel 495
  pyrites 495
  soap 499
Arsenicum 495
  vapor density of 44, 495
  history, natural history, preparation, properties, uses 495, 496
Arsenides, The 310
Arsenide 495
"Arsenite" 498
Arsenites, The 499
Arsenious acid 496, 498
  —solubility of 499
  —varieties of 498

PAGE
Arsenious acid—*continued.*
  —antidotes for 499
  —reactions of compounds of 501
  Fleitmann's test for 497
  Marsh's test for 479, 503
  Reinsch's test for 503
  Hoffmann's test for 497
  anhydride 496, 498
  bromide 496, 502
  chloride 496, 502
  disulphide 496, 500
  fluoride 502
  hydride 311, 497
  —solid 497
  iodide 496, 502
  oxychloride 502
  pentafluoride 496, 503
  sulphide 496, 501
Arseniuretted or arsenetted hydrogen 496, 497
Arsine 497
Arsines, The 763
Artiads or evens 48, 52
Artificial gum 689
Asparagin 776
Assamar 682
Atacamite 460
"Ate," the termination 29
Atmolysis 230
Atmosphere as a natural disinfectant 588
Atmospheric air (*See* Air).
Atom, definition of 32
Atomic heat 46
  theory 31, 32
  weight (definition of) 33
Atomic weight, relation between, and specific gravity 44
  and specific heats 45
  —by Avogadro's law 38
  —by specific heat 46
  volume 44
Atomicities, table of 51
Atomicity or quantivalence 47
  method of determining 49
  latent, active, and absolute 52
Atoms 32
Atropine 775
  tests for 781
Aurates, The 507
Auric anhydride 506, 507
  chloride 506
  cyanide 607
  hydrate 506, 507
  oxide 506, 507
  potassic chloride 508
  sulphide 506, 508
Auricome 249
Aurous chloride 507
  iodide 507
  oxide 506, 507
Austrapyrolene 649
Austraterebenthene 649
Avogadro's law 38
  apparent exceptions to 38

PAGE
Azolitmine 783
Azote (nitrogen) 115
Azotyl. 131
    chloride and bichloride of . . . 148
    bichloride (chloro-nitric gas) . 148
    chloride (nitrous oxychloride) . 147
Azurite 453

B.

Baldwin's phosphorus 149
Ball soda 358
Balsam of Peru 713
Balsams 654
Barilla 357
Barium 374
    history, natural history, preparation, properties 375
    compounds of 375
    spectrum of 377
    reactions of the compounds of . 377
    bromide 375, 376
    carbonate 375, 377
    chlorate 375, 377
    chloride 375, 376
    chromate 412
    dichromate 412
    dioxide 376
    dithionate 189, 320, 375
    ferrate 407
    fluoride 375
    hydrate 375, 376
    iodide 375
    manganate 395
    molybdate 516
    nitrate 375, 377
    nitrite 375
    osmate 476
    oxide 14, 375, 376
    perchlorate 375
    permanganate 396
    peroxide (dioxide) . . 14, 375, 376
    persulphate 188
    phosphates of 375
    pyrosulphate 375
    selenate 314
    silicofluoride (fluosilicate) 257, 336, 375
    sulphate 187, 375, 377
    sulphide 375, 376
    sulphite 375
    sulphydrate 376
    tellurate 197
    thiosulphate 191, 375
    vanadate 504
Barometer, table of the corresponding heights of the, in millimetres and English inches . . 843
Baryta (barium oxide) . . . 171, 376
    caustic (barium hydrate) . . . 376
    water 376
Baryto-calcite 338
Basalt 443
Base, definition of a 74, 294
Bases, action of, on salts in solution 9
    varieties of 294
    produced by action of ammonia on the chlorides of platinum . 513
    effects of heat upon 6
Bassorin 689
Batteries, secondary 20
    storage 20, 526
Baumé's hydrometer, specific gravities corresponding to degrees of 840, 841
Bauxite 437, 440
Bay salt 355
Beeswax 705
Bell metal 456, 480
Benzaldehyde 746
Benzamide 760
Benzene . . . 274, 592, 595, 634, 638
    preparation, properties 638
Benzenes, The 634
    preparation, properties 635
    chlorides 638
    derivatives of 639
Benzerythene 638
Benzoic anhydride 714
    chloride 713
    oxide 714
    peroxide 714
Benzol (*see* Benzene).
Benzoline 755
Benzonitrile 762
Benzophenone 642
Benzoyl chloride 713
    glycocoll 829
Benzyl-benzene 642
    ethylbenzene 642
    metaxylene 642
    paraxylene 642
    toluene 642
Benzylamine 753
Berberine 776
Berthelot, law of maximum work in thermo-chemistry 17
Berthollet, on the influence exerted by quantity on affinity . . . 11
Beryl 447
Beryllium 447
    aluminate 439
    aluminic silicate 335, 447
    bromide 448
    carbonate 448
    chloride 448
    fluoride 448
    hydrate 448
    nitrate 448
    oxide 448
    phosphate 448
    silicate 335, 448
    sulphate 448
    sulphide 448
    general properties of 447
    reactions of the compounds of . 448
Bessemer steel process 401
    slag 504
Bezoar stones (Oriental) 823

PAGE
Bicarbonates, The 337
Bichromates, The. 414
Bile 822
  average composition of, per 1,000 parts 822
Bilin 822
Biliphæin 823
Bilirubin. 823
Biliverdin 823
"Bin," "ter," etc., the prefixes . . 29
Binary theory of salts 292
Binoxalates, the 337
"Biscuit" (earthenware) 445
Bismuth 464
  natural history, preparation, properties, uses 464
  compounds of 465
  reactions of the salts of . . . 467
  sesquioxide or trioxide of . . . 465
  subnitrate or trisnitrate of . . 467
  trichloride of 466
Bismuth glance 464, 467
  ochre 464, 465
Bismuthic oxide 465
  acid 465
  anhydride 465, 466
  hydrate 465, 466
  nitrate 465
  sulphate 465
  sulphide 465, 467
Bismuthines 733
Bismuthite 464
Bismuthous bromide 465
  bismuthate 465, 456
  chloride 465, 466
  fluoride 465
  iodide 465
  nitrate 467
  oxide 465
  oxybromide 465
  oxychloride 465
  oxyiodide 465
  sulphate 465
  sulphide 465, 467
  telluride 196, 464
Bisulphates, The 337
Bitter almond oil 746
Bittern, the mother liquor of sea water 355, 389
Bitumene 638
Bixine 784
Black ash 358
Black band 399
  jack 422
  wash 543
Black coloring matters 786
Blacklead 199
Blast furnace 400
  —gases from the 208, 400
Bleaching powder 328, 385
Blende 171, 418
Blister copper 454
Blood 803
  composition, constitution, 804; properties, 805.
Blood—*continued.*
  coloring matter of . . . 399, 805
  liquor sanguinis 813
  water in 814
  changes in, effected by respiration 81
  coagulation of the 807
  temperature of the 806
  specific gravity of the 806
  odor of the 806
  alkalinity of the 814
  albumen, fibrin, fatty matters, extractive matters, mineral matters in 814-816
  average composition per 1,000 parts of human 805
  free gases present in 100 vols. of, taken from the carotid of a dog 804
  origin of the 809
  corpuscles 810
  average composition of 1,000 parts of, and of liquor sanguinis 805
  crystals 813
Bloodstone 406
Blue coloring matters 785
  copper 461
  copperas 461
  malachite 453
  stone 461
  verditer 462
  vitriol 461
Bog iron ore 399
Boiled oil 732
Boilers, furring in 585
Boiling points, definition of . . . 237
  influence of pressure on . . . 237
  relation to molecular weight . . 47
Boiling point of water, variations in 237
Bolognian phosphorus . . . 149, 376
Bonds, Frankland's views of . . 46
Bone, properties of 800
  action of heat, of water, of acids, of burial on 801
Bone-ash 801
Bone black 199, 801
Bone calculus 385
  earth 832
Bone oil 801
Bones of a child and an adult, composition of the healthy human 799
  of different mammals, birds, fishes, and reptiles, composition of 799
  composition of certain diseased . 800
Borates, The 336
Borax (sodic biborate) 361
Boric bromide 220
  chloride 220
  ethide 766
  fluoride 220
  hydride 279

PAGE
Boric—*continued.*
methide 766
nitride 218, 220
sulphide 221
Borides, The 311
Borneène 652
Borofluorides, The 221
Boron 218
history, natural history, varieties, preparation, properties . . . 218
(amorphous) 218
(crystalline) 218
(diamond) 218
(graphoidal) 218
Boyle, law of 118
Boyle and Mariotte, law of . . . 39
” ” ” ” in respect to hydrogen 229
Boyle's fuming liquor 370
Brain and nerve tissue . . 157, 803
Brass 420, 429
Braunite 391, 393
Braziline 785
Bread-making, alcoholic fermentation in 586
Dauglish's process of 586
Brewer's grains 585
Brewing, alcoholic fermentation in 585
Brimstone 171
Brine 355
Brin's process for preparing oxygen 70
Britannia metal 480, 488
British gum 689
Brittleness, meaning of 282
Brochantite 462
Bromates, The 325
Bromethylene 274
Bromides, The 304
definition, natural history, preparation, varieties, properties, 304 ; tests, estimation, uses . 305
oxy- 305
Bromine 102
preparation by process of Desfosses 103
hydrate 104
compounds with oxygen . . . 104
—with chlorine 105
—with iodine 112
estimation of, with chlorine and iodine in an organic body . . 567
Bromoform 628
Bromous chloride 105
Bronze 290, 480
coinage 456
powder 483
Brookite 484
Brown coloring matter 786
hæmatite 399
iron ore 399
sulphuric acid 182
Brucine 774, 781
Brunswick green 460
black 596

PAGE
Brushite 385
Burgos lustre 508
Burgundy pitch 653
Burnett's disinfecting fluid . 422, 589
Butane 624
Butters, metallic 301
Butylamine 753
Butylbenzene 637
Butylene 630
glycol 672
Butyrone 748

C.

Cacodyl (kakodyl) 764
Cadet's fuming liquid 764
Cadmium 468
history, natural history, properties, uses ; compounds with oxygen, with the haloids, and with sulphur 468
reactions of the salts of . . . 469
vapor density of 44
Cadmium bromide 468, 469
carbonate 468
chloride 468, 469
hydrate 468, 469
iodide 468, 469
nitrate 468
oxide 468, 469
sulphate 466, 469
sulphide 468, 469
Cæsium 366
carbonate 366
chloride 366
hydrate 366
nitrate 366
oxide 366
platinic chloride 366
sulphate 366
—hydric 366
Caffeine 774
tests for 781
Cairngorm, crystalline variety of silica 222
Cajuputol 651
Calamine 418
electric 418, 423
Calcined magnesia 388
Calcite 384
Calcium 379
history, natural history, preparation 379
compounds of 380
spectrum of 386
reactions of the salts of . . . 386
bromide 380
carbonate 380, 384
chlorate 351
chloride 380, 382
—boiling point of saturated solution 238

PAGE
Calcium—*continued.*
  chlorohypochlorite 386
  chromate 412
  disilicide 380
  disulphide 380, 383
  dithionate 320, 380
  fluoride 380, 383
  hydrate 380, 381
  hypochlorite 328, 380, 385
  hypophosphite 380
  iodide 380
  magnesic silicate 335
  molybdate 516
  nitrate 380, 384
  oxalate 380, 385, 720
  oxide 380, 381
  pentasulphide 380, 383
  peroxide (dioxide) 380, 381
  persulphide 359
  phosphate 164, 380, 385
  phosphide 380
  potassium sulphate 380
  pyrolignate 598
  silicates 335
  sodium sulphate 380
  sulphate 380, 383
  sulphide 380, 383
  sulphite 95, 380
  sulph hydrate 383
  superphosphate 385
  —solubility of 241
  thiosulphate 188, 359, 380
Calc spar 379, 384
Calendulin 689
Calico, grass-bleaching of 590
Calico-printing 787
Calomel (mercurous chloride) 538, 542
Calx 68
Camphine (Boston turpentine) 648
Camphol 652
Camphor, common 651
  as a disinfectant 589
  Borneo 652
  artificial 599
  oil of 651
  —liquid 651
Camphors 651
Candles 735
Cannabin 653
Cannel gas 275
Canton's phosphorus 383
Caoutchine 655
Caoutchouc 655
Capillary pyrites 430
Caproates, The 705
Capsicum resin 653
Caramel 682
Carbamide 708, 761, 826
Carbamine 630
Carbamines, The 762
Carbides, The 285, 310
Carbimide 761
Carbinol 658, 662
Carbinols, The 658
Carbo-hydrates, The 680

PAGE
Carbolic acid, to distinguish, from kreasote 671
Carbon 198
  synonym, history, natural history, 198; varieties, 199; preparation, 200, 201; properties, 201, 204.
  chemistry of, a definition of organic chemistry 557
  latent heat of the vapor of 16
  compounds with oxygen 208
  — with the haloids 214, 272
  — with oxygen and the haloids 216
  — and sulphur 216
  —experimental determination of the carbon, hydrogen and oxygen in an organic compound not containing nitrogen 563
  estimation of the hydrogen and carbon in a body containing nitrogen 564
  chemistry of carbon and its compounds, (Laurent's definition of organic chemistry) 557
  specific heat of 200
  specific gravity of 201
  crystalline form of 201
Carbon, a grouping agent in non-nitrogenized bodies 559
  daily consumed as food, and daily evolved as carbonic acid 82
  consumed per hour by males 83
  of gas retorts 199, 200
  (amorphous) 200
  (or carbonic) dioxide 201
  bichloride of 214
  sesquichloride of 215
  protochloride of 215
  bisulphide of 216
  tetrachloride 628
  monoxide 208
Carbonates, The 334
  definition, natural history, 334; preparation, properties, tests, uses, 335
  double 338
  sulpho- 308
Carbonic acid 210, 214, 592
  anhydride 210
  —synonyms, history, 211; natural history, 211; preparation, 211; properties, 212-214; tests 214
  —proportions of, in the air 125
  —produced, and air vitiated per hour 126
  —heat developed in formation of, from carbon 16
  —physiological action of 212
  —dissociation of 213
  —action on flame of 214
  —absorption coefficient of 242
  chlorobromide 215
  dibromide 215
  dichloride 215
  disulphide 4, 216, 592

PAGE
Carbonic—*continued.*
  monochloride 215
  —synonyms, preparation, properties 215
  oxide 208, 592
  —synonyms, history, natural history, preparation, 208; properties, 209.
  —absoption by carbon 204
  —absorption coefficient of . . . 242
  —physiological action of . . . 209
  —hæmoglobin 821
  oxychloride 216
  oxysulphide 217
  subchloride or hexachloride . . 215
  tetrabromide 215
  tetrachloride of 214
  tribromide 215
  trichloride 215
Carbonyl chloride 216
Carboxyl 693
Carburetted hydrogen . . . 271, 272
Carmine 785
Carnallite 340, 344, 389
Carragenin 689
Carré's ice-making apparatus . . 260
Carthamine 785
Carvene 651
Carvol 651
Case-hardening 345, 402
Casein 796
Cassel green (barium manganate) 395
Cassiterite 478
Castile soap 735
Cast iron 400
Castorin 653
Catalysis, an assumed new force 12, 13, 249, 584
Caustic potash 342
  soda. 354
  baryta 376
Cedriret 597
Celestine (strontium) . . . 171, 378
Cellulin 789
  preparation, properties; action of acids; uses 789, 790
Cellulo-nitrin 790
Cellulose 789
Cements, or hydraulic mortars . . 382
Cement, Roman 382
  Portland 382
  Scott's 382
Centimetres, to reduce cubic, to cubic inches 843
Cerasin 689
Cerebrin 803
Ceric fluoride 450
  hydrate 450
  nitrate 450
  oxide 450
  sulphate 450
Cerin 698
Cerite 450
Cerium 449

PAGE
Cerotene 630, 657
Cerous chloride 450
  fluoride 450
  nitrate 450
  sulphate 450
Ceruse, or white lead 528
Cerussite 520
Cetene. 630
Cetin 734
Chalcedony, an amorphous variety of silica 221, 223
Chalcolite 431
Chalk 384
Chalk-stones 827
Chalybeate waters 410
Chamber, sulphuric acid 182
Charcoal 198
  absorption of gases by 203
  —of aqueous vapor by 203
  as a disinfectant 205, 589
  as a fuel 205, 208
  use in medicine 208
  animal 199, 201
  vegetable 200, 205
  wood 199, 200
  for gunpowder 349
Charles, law of 40
Chemical action (*see* Affinity) . . 1
  combinations 1
  equations 31
  formulæ 30
  homogeneity. 2
  mixture 2
  nomenclature 27
  symbols 30
Chemism. 1
Chemistry, organic 556
  —definitions of 556
Chessylite 463
Chili saltpetre 360
China 446
China clay 444
China stone. 446
Chinese wax 698, 718
Chinoline. 754
Chittin 686
Chloral 665, 745
Chloral hydrate 745
Chloralum 440, 589
Chlorates, The. 325
Chlor-aurates, The 508
Chloric dioxide 99
  peroxide 99
  —synonyms, history, preparation, properties 99
Chlorhydrin. 740
Chlorhæmatin 812
"Chloride of lime" 99
Chlorides, The 300
  definition, natural history, preparation, 300; varieties, 301; properties, 301; tests, 302; estimation and uses, 303
  double 302
  oxy-. 290-302

PAGE

- Chlorine 13, 88
  - synonyms, 88; history, 88; natural history, 88; preparation, 88-90; properties, 90-94; tests, 94; estimation, 94; uses, 94.
  - hydrate 7, 92
  - monoxide 96
  - compounds with oxygen . . . 95
  - —with iodine 112
  - —with nitrogen 145
  - —with nitrogen and oxygen . . 147
  - —with oxygen 95
  - —with sulphur 191
  - estimation of chlorine, bromine, and iodine in an organic body 567
  - bleaching power of . . . 93, 94, 98
  - as a disinfectant 94, 95
  - as a medicinal agent 95
  - vapor density of 90
  - absorption coefficient of. . . . 242
  - action on metals 92, 94
  - —hydrogenous compounds . . 92
- Chlor-isatin 93, 785
- Chlorite (an aluminium silicate) . 443
- Chlorite, distinction between a, and a hypochlorite 328
- Chlorites, The 99, 327
- Chlorochromates, The . . . 316, 417
- Chloroform 628, 629, 665, 745
- Chloro-nitric gas 148
  - —synonyms, preparation, properties 148
- Chloro-nitrous gas (nitrous oxychloride) 147
- Chloropal 335
- Chloropernitric gas (nitrylic chloride). 148
- Chlorophyll 399, 786
- Chloropicrin 630
- Chloroplatinites, The 512
- Chloro-platinates, The 512
- Chlorostannates, The 483
- Chlorotoluene 637
- Chlorozone as a disinfectant . . . 589
- Choke damp. 210
- Cholesterin 672, 803, 833
- Cholin. 803
- Cholophæin 823
- Chondrin. 802
- Chrom-amine 414
- Chromates, The 315, 414
  - definition, tests 315
- Chrome, alum 412, 416, 417
  - iron ore 411
  - iron slate (stone) 411
  - orange 416
  - ochre 415
  - red 416
  - yellow 315, 416
- Chromites, The 413
- Chromium 411
  - history, natural history, preparation, properties 411
  - compounds of 412
  - reactions of the salts of . . . 418

PAGE

- Chromium—*continued.*
  - fluorides of 412, 417
  - sesquichloride of 416
  - sesquioxide of 413
  - potassium sulphate . . . 412, 417
- Chromic anhydride 412, 414
  - chloride 412, 416
  - hydrate 412, 413
  - nitrate 412
  - nitride 412
  - oxide 412, 413
  - oxychlorhydrate 412, 417
  - oxydichloride 412, 417
  - perfluoride 412, 417
  - peroxide 412
  - sesquisulphide 417
  - sulphate 412, 417
  - sulphide 412, 417
- Chromous chloride 412, 416
  - carbonate 412
  - hydrate 412, 413
  - oxide 410, 412
  - phosphate 412
  - potassic sulphate 412
  - sulphate 412
- Chromous salts, action of nitric oxide on 132
- Chromyl 414
- Chrysaniline 759
- Chrysene 592, 597, 638
- Chrysoberyl 439, 447
- Chrysoquinone 646
- Chyle and lymph 816
  - percentage composition of. . . . 817
- Cinchona bark, alkaloids of . . . 772
- Cinchonicine 772
- Cinchonidine 772
- Cinchonine 772
  - tests for 780
- Cinnabar. 171, 538, 547
- Cinnamene 640, 717
- Citramide 761
- Citrates, The 725
  - double, The 338
- Citrimide 761
- Clark's process for softening water 385
- Clay 437, 443
  - formation, composition, varieties, properties 443, 444
- Clay iron-stone 399, 410
  - Medway 382
- Coagulated proteid 797
- Coagulation of the blood 807
- Coal 205
  - composition of various kinds of 206
  - amount of sulphur in different varieties of 206
  - anthracite or steam coal . . . 206
  - ash of 206
  - burning of, in close vessels and in the open fire 206, 207
  - formation of 205
  - products formed by the action of heat on 206, 592
  - — —by the distillation of . 592, 593

PAGE
Coal-gas 275, 593
  composition of 275, 593
  liquor 595
  manufacture of 593
  naphtha 595
  purification of 276, 406
Coal-tar 595
  —creasote 670
  —dyes 758
Coarse metal (copper) 454
Cobalt 424
  history, natural history, preparation, properties 424
  ammonium compounds of 427
  compounds of 425
  reactions of the salts of 428
  arsenide of 424
  arseno-sulphides of 424
  protoxide of (cobaltous oxide) 425
  sesquioxide of (cobaltic oxide) 426
  silicates of 425, 427
  vitriol 426
  tin white 424, 495
  glance 495
  speiss 424
Cobaltamines, The 427, 513
Cobaltic chloride 425, 426
  hydrate 425, 426
  oxide 425, 426
  sulphides 425, 426
Cobalticyanides, The 614
Cobalticyanogen 614
Cobaltous arsenate 425
  bromide 426
  carbonate 425, 427
  chloride 425, 426
  cyanide 607
  fluoride 426
  hydrate 425
  iodide 426
  nitrate 425, 426
  oxalate 424, 425, 427
  oxide 425
  phosphate 425, 427
  silicate 427
  sulphate 425, 426
  sulphide 425, 426
Cobalto-cobaltic oxide 425, 426
Cocaine 775
Coccinite 546
Cochineal 785
Cocoa-nut carbon 204
Codeine 773, 774
Cod-liver oil, iodine in 106
Cœrulignone 597
Cohesion, attraction between similar molecules 1
  modifies chemical action 4
Coke 199, 206, 207
Colcothar 181, 405, 409
Cold, influence of heat and, on affinity 14, 15, 588
Collidine 754
Collodion 790
Colloids 224, 240

PAGE
Colophene 649
Colophony 653
Coloring matters 783
  —power of carbon for absorbing 204
  —used for glass and porcelain 364
Colza oil 711
Combination, atomic and molecular 36, 41
  laws of 35
  molecular 36, 41
  volume 41
  weight 35
Combining proportions, 31; affinity measured by 24
Combustibles 276
Combustion, use of oxygen as an agent in 84
  supporters of 276
  slow and rapid 276
Common salt 355
Compound radicals, chemistry of 32, 36, 58, 557, 605
Compounds, elements and 27
Concrete 382
Concurring attractions 12, 14
Condy's green disinfecting fluid 316, 395
  red disinfecting fluid 396
Coniferin 687
Conine 754, 770, 771
Constant proportions, laws of 35
Constitution, water of 244, 337
Contact decomposition 12
Converted nitre 248, 360
Convolvulin 687
Copal 653, 654
Copper 453
  natural history, preparation, impurities, properties, uses, 453 to 456
  alloys of 456
  amalgam 539
  ores of 453
  glance 453, 461
  compounds of 457
  —and hydrogen 457
  —and oxygen 457
  —and chlorine 459
  —and sulphur 461
  oxysalts 461
  reactions of the salts of 463
  pyrites 171, 453, 461
  black oxide of 458
  chloride of 460
  monoxide 458
  subbromide of 460
  subchloride of 459
  suboxide or red oxide of 457, 458
  subsulphide of 461
  sulphate of 461
  sulphide of 461
  smelting 453
  smoke 454
  roasting 172, 454
  furnace, gases of 208

PAGE
Copper—*continued.*
  action of water on 228
  tile 454
  blistered 455
  dry 455, 458
  poled 455
  zinc couple 603
Copperas 409
Coprolites 150, 385
Coquimbite 410
Coral 384
Coridine 754
Corky matter 789, 791
Cornelian, amorphous variety of silica 123
Corrosive sublimate 544
Corundum 437
Cotunnite 526
Covellin 461
Cream of tartar 351, 490, 722, 723
Creasote, to distinguish carbolic acid from 671
Cresol (*see* Acid cresylic).
Creusot ironworks 504
Crith, function of the 43
Critical point 212, 237
Crocus of Mars 405
Crookesite 550
Crotonylene 633
Crum's test for nitric acid 145
Cryohydrates 8
Cryolite 86, 440
Crystallization; fractional 3
  water of 244
Crystallography 65
Crystalloids 224, 240
Crystals, definition of 65
  of leaden chamber 147, 182
  of Serullas 101
  systems of 65
  methods of preparing 65
Cubic nitre 360
  system of crystals 65
Cudbear, preparation of 783
Cumene (mesitylene of coal tar oil) 592, 595, 634
Cupellation, process for extracting silver 521
Cupr'ammonia 456, 459
Cuprammonic chloride 460
  sulphate 462
Cupric acetate 702
  arsenate 332, 457, 462
  arsenite 334, 457, 462, 499
  bromide 460
  carbonate 457, 463
  chloride 20, 457, 460
  ferrocyanide 463, 613
  fluoride hydrate 457, 458
  hydrate 457
  hydride 457
  iodide 457
  nitrate 457, 462
  nitride 310, 457, 460
  oxides 457, 562

PAGE
Cupric—*continued.*
  oxychloride 457, 460
  oxysalts 461
  pentasulphide 457, 461
  phosphate 457, 463
  phosphide 457, 461
  selenide 194, 457
  silicate 457
  sulphate 244, 457, 461, 589
  —compounds with ammonia 462
  sulphide 457, 461
Cuproso-vinyl oxide 275
Cuprous acetylide 275
  arsenide 457, 497
  bromide 457, 460
  chloride 20, 457, 459
  —absorption of carbonic oxide by 210, 459
  —test for acetylene 275
  ferric sulphide 461
  fluoride 457
  hydrate 457, 458, 463
  hydride 311, 457
  iodide 457, 460
  nitride 457
  oxide 457
  phosphide 457
  quadrantoxide 458
  sulphide 457, 461
Curds 818
Currying, mode of 737
Cusso bark 772
Cuttle fish, copper in blood of 453
Cyamelide 610, 611
Cyanates, The 610
Cyanides, The 608
  preparation of metallic cyanides, properties, uses, 608, 609.
  double, The 613
  tests for 619
Cyanine 784 785
Cyaniline 757
Cyanite 443
Cyano-ethane 628
Cyanogen 202, 604
  derivation, history, natural history, preparation, properties, 604, 605
  chlorides of 60, 607, 609
  cyanides, chlorides, bromides, iodides, sulphide, and hydroxides of 607
  double salts of 613
  bromide 610
  iodide 610
  sulphide 610
Cyano-methane 628, 629
Cyano-paraffins 629
Cydonin 689
Cymene 597, 634, 652
Cymidine 754
Cymylamine 753
Cystine 831

D.

PAGE
Dalton, theory of 32
Dammar resin 653
Daniel's hygrometer 123
Dark red silver ore 530
Deacon's process for preparing chlorine 89
Dead ore 595
Dead Sea water 102
Decane 624
Decay, conditions necessary for 590
Decene 630
Decine 633
Decipium 451
Decomposition, artificial, of organic bodies 591
  contact 12
  of a compound, affinity measured by the amount of force required to effect the 22
Deliquescence 244
Density of bodies increased by affinity 3
  maximum, of water 239
Deodorizers 588
Dephlogisticated air 68
  marine acid gas 88
Dephlogisticated nitrous air 128
Derbyshire spar 86
Desfosses' process for the preparation of bromine 10
Destructive distillation 591
Devitrification of glass 364
Dew, analysis of (Russell) 123
  point 123
  bleaching action of 77
Dewar on liquid oxygen 73
  physiological action of ozone 78
  on hydrogenium 231
Dextrin 689
Dextro-glucose 684
Dextrose 684
Dhil mastic 525
"Di," "tri," "tetra," etc., the prefixes 29
Diacetamide 760
Diadelphic or methyl type 559
  condensed or olefine type 560
Diallyl 633
Diallylamine 752
Dialysis 240, 576
Diamagnetics 284
Diamines 750, 754
Diamond, the 198, 199, 200
Diamylamine 752
Diamylene 630
Diaspore 438
Diastase 581, 585, 689
Diathermanous, definition of 356
Dibenzyl 642
Dibenzylamine 753
Dibrom-anthra-quinone 644
Dibromobenzene 639

PAGE
Dibutyl 624
Dibutylamine 753
Dibutyraldine 771
Dichlorethane 273
Dichlorobenzene 639
Dichlormethane 628
Dicymylamine 753
Didymium 450
Didymic oxide 450
Didymous chloride 450
  hydrate 450
  nitrate 450
  oxide 450
  sulphate 450
Diethyl 624
Diethylamine 752
Diethylbenzene 634
Diethyl methylbenzene 634
Diethyl phosphine 763
Diffusion 2, 230
  of gases 76, 230
  of liquids 240
Diffusiometer of Graham 230
Digestion, and the fluids concerned in the process 819
Dihydric disulphate 183
  disulphide 269
  selenide 270
  sulphate 181
  sulphide 266
  tetrathionate 190
  trithionate 190
Dimethylamine 752
Dimethylbenzenes 634, 636
Dimethyl phosphine 763
Dinaphthyl 641
Dinitric pentoxide 139
Dinitrobenzene 639
Diorite 443
Diopside 335
Diothene 443
Diphenyl 638, 642
Diphenylbenzene 646
Diphenyl methane 642
Diphosphoric tetrasulphide 193
Dippel's oil 801
Dipropargyl 634
Disinfectants, natural 588
  artificial 588
Disinfection 589
Dissociation 15
Distillation 233
  destructive 591
  fractional 3
Disulpho-dithionic acid 190
Dithionates, The 189, 320
Ditolyl 642
Dixylylamine 753
Dobereiner's lamp 10
Dodecane 624
Dolomite 338, 389, 390
Dolerite 443
Draconine 785
Dragon's blood 653
Drying-oil 732

PAGE
Dry rot 791
Dualistic theory of salts 292
Ductility of metals 282
Dulcin 679
Dulcite 679
Dulcose 679
Dulong and Petit, law of 47
Dumas' process for estimating nitrogen in an organic body 565
"Dunging" 788
Dung substitutes 362, 500
Durkheim springs, cæsium and rubidium in the 360
Dutch liquid 273
  metal 94
Dyads 50
Dyeing and calico-printing 787
Dynamicity 47

E.

Earth, constituents of the solid crust of the 69
Earthenware, manufacture of common 445
Ebullition 237
Efflorescence 244
Eggshell, composition of 379, 384
Elaldehyde 745
Elastic power of gases 237
Elasticity modifies chemical action 5
Elayl (ethylene) 272
Elective gravitation 1, 2
Electric calamine 418
Electro gilding 507
  negatives 2, 19
  positives 2, 19
Electrical properties of metals 283
Electrolysis 18
  —laws of 19
  of water 233
Electrolyte 18
Electro silvering 531
Electrum 505
Elements and compounds 27
Embolite 530, 534
Emerald 335, 338, 447
Emery 438
Emetin 772
Empyreal air 68
Emulsin 581
Enamelling glass 364
Epsom salts 389
Equations, chemical 31
Equivalents (Faraday) 19
Erbia 451
Erbium 451
Eremacausis, or slow oxidation, 77, 81, 590
  conditions necessary for promoting 590
  circumstances influencing 591
Ergotin 653

PAGE
Erythrite 657, 666
Ethal 657, 733
Ethane 624
Ethene (ethylene) 592, 630
Ethenyl nitrite 695
Ether 740
  allylic 738
  amylenic 740
  amylic 738
  benzylic 738
  boracic 766
  butylic 738
  ethylenic 740, 741
  ethylic butylic 738
  ethylic (ether) 738, 740
  glycylic 741
  methylic 738
  methylic amylic 738
  methylic ethylic 738
  phenylbenzylic 738
  phenylic 738
  propylenic 740
Ethereal salts 632, 661, 694, 742
Etherene (ethylene) 272
Ethers. The 738
  compound 742
  haloid 741
  sulpho- or thio- 741
  oxy- 738
  preparation of the 739
  —of methylic series 739
  —of venylic series 739
  —of benzylic series 739
  of monohydric alcohols 738
  of dihydric alcohols 740
  of trihydric alcohols 741
Ethine (acetylene) 274, 592, 633
Ethylamine 599, 752
Ethylamylamine 753
Ethylbenzene 634, 636, 637
Ethyldimethylbenzene 634
Ethylene, or heavy carburetted hydrogen 272, 630
  synonyms, history, natural history, 272; preparation, properties, 273
  diamine 755
  glycol 673
  action of palladium on 471
  bromide 274
  chloride 273
  iodide 274
Ethylenic butyrate 742
  cyanide 628
  isosulphocyanide 613
  nitrite 742
  oxalate 720
  oxide 741
  urea 755
Ethylic acetate 703, 742
  acetamide 760
  alcohol (*vide* Alcohol).
  aldehyde (*vide* Aldehyde).
  hydride 272, 624
  sulphydrate 679

PAGE
Ethyl naphthalene 640
  phosphine 763
Ethyloxide 740
Eucalyn, an unfermentable sugar 686
Euchlorine 96, 102
Eupione 597
Eustatite 335
Evens or artiads 52
Everitt's white salt 613, 618
Excrementitious products of the body 824
Excretin 832
Explosions, theory of gunpowder 350

F.

Fæces 832
Fats and oils 731
  definition, natural history, preparation, classification 731
  fixed and volatile 731
  table of 733
Fat of the bay tree 698
  —cocoa bean 706
  of pichurim beans 698
  otaba 698
Fatty acids, supplement to the 731
Fatty series of acids 696, 697
Feathers, copper in 453
Felspar 335, 338, 340, 443
  calcium 443
  lithium 443
  potash 443
  sodium 443
Ferment diseases 582
Fermentation 578
  varieties of 579
  conditions necessary to produce 581
  circumstances influencing 583
  theories to account for 584
  practical applications of the processes of 585
  acetous (so called) 580, 586
  alcoholic or vinous 579, 586
  butyric 580
  lactic acid 579, 586
  mucous or viscous 580
Ferments 12, 581
Fer oligiste 399
Ferrates, The 407
Ferric salts, reactions of 411
Ferric acetate 702
  acid 404, 407
  anhydride 404, 407
  bromide 404, 408
  chloride 404, 407
  cyanide 607
  disulphide 408
  ferrocyanide 411, 617
  fluoride 404, 408
  hydrate 404, 406
  iodide 404, 408
  nitrate 405, 410

PAGE
Ferric—*continued.*
  nitride 404
  oxalate 720
  oxide 404, 405
  phosphate 405, 410
  silicate 410
  sulphate 405, 410, 589
  sulphide 404, 408, 409
Ferricyanides 616
  tests for the 620
Ferricyanogen 614
Ferrocyanides 614
  —tests for the 620
Ferrocyanogen 614
Ferroso ferric oxide 406
  —hydrate 407
Ferrous salts, action of nitric oxide 132
  reactions of 410
Ferrous acetate 702
  bromide 404, 408
  carbonate 405, 410
  chloride 404, 407
  chromite 413
  cyanide 607
  ferricyanide 411, 617
  fluoride 404, 408
  hydrate 404, 405
  iodide 404, 408
  nitrate 405, 410
  oxalate 405, 410, 720
  oxide 404, 405
  phosphate 164, 405, 410
  silicate 335, 405, 410
  sulphate 405, 409
  sulphide 404, 408
Fibrin 796, 814
Fibrinogen 795, 808
Fine metal (copper) 454
Fire clay 444
  damp 211, 271, 629
Fish scales, composition of 800
Fixed air 210
Flame, chemistry of 276
Fleitmann's test for arsenic 497
Flesh, composition of 801
  juice of 801
Flint; amorphous variety of silica 221
Fluocerite 450
Fluor spar (calcic fluoride), 86, 379, 383
Fluoricum 86
Fluorides, The 305
  definition, natural history, preparation, properties 305
  niobo- 306
  silico- 306
  stannico- 306
  tests, estimation, and uses 306
  thoro- 306
  zircono- 306
Fluorine 86, 87
  compounds of nitrogen with 145
  compounds of silicon with 225
Fluosilicate, potassium 257
Fluosilicates, The 257, 306, 336
Fly powder 496

PAGE

- Force, mechanical, may modify chemical action . . . 12
  - vital, so called influence on chemical action . . . 20
- Force . . . 1
- Formates, The . . . 701
- Formonitrile . . . 762
- Formulæ, chemical . . . 30, 572
  - constitutional . . . 34
  - experimental or empirical . . . 55-572
  - graphic . . . 48
  - molecular . . . 33, 573
  - rational or theoretical . . . 56
  - glyptic . . . 48
- Formyle, chloride of . . . 629
- Fowler's solution . . . 334, 500
- Fractional precipitation . . . 3
  - crystallization . . . 3
- Frankland's constitutional formulæ . . . 48
- Franklinite . . . 418
- Fruit, ripening of . . . 792
- Fuller's earth . . . 443
- Fulminates . . . 612
- Fulminating gold . . . 508
  - silver . . . 533
  - mercury . . . 542
- Furfuramide . . . 755
- Furfurine . . . 755
- Furfurol . . . 682
- Fusel oil . . . 657
- Fusible calculus . . . 832
  - metal . . . 4, 291, 464
- Fusibility, alterations, the result of chemical action . . . 4

G.

- Gadolinite . . . 451
- Gahnite, a zincic aluminate . . . 418, 439
- Galactose . . . 683, 685
- Galena . . . 171, 520, 527
  - silver in . . . 530
- Gall-stones . . . 823
- Gallium . . . 446
  - history, occurrence, preparation, properties . . . 446
  - —reactions of the compounds of . . . 447
  - alum . . . 447
  - chloride of . . . 447
  - oxide of . . . 447
  - sulphate of . . . 447
- Gamboge . . . 784
- Garnet . . . 443
- Garnierite . . . 429
- Gas, the word adopted by Van Helmont . . . 118
  - a homogeneous as distinguished from a non-homogeneous . . . 2
  - carbon . . . 199, 200, 593
  - chloro-nitrous . . . 147
  - coal (*see* Coal gas).
  - fatiginosum . . . 118

PAGE

- Gas—*continued.*
  - inflammable . . . 227
  - liquor . . . 595
  - marsh, series . . . 271
  - olefiant, series . . . 272
  - phosgene . . . 18, 36, 216
  - pinque . . . 118
  - pit . . . 271
  - siccum . . . 118
  - sylvestre . . . 118, 131, 210
  - water . . . 210
- Gases, relative weights of compound and elementary . . . 42
  - power of carbon for absorbing . . . 203
  - absorption of . . . 7, 241
  - adhesion of, to solids . . . 10
  - solubility of . . . 7, 241
  - free, in urine . . . 830
  - diffusion of . . . 76, 230
  - expansion by heat of . . . 212
  - liquefaction of . . . 212, 237
  - —relation to pressure . . . 212
  - action of solvents on a mixture of . . . 243
- Gastric juice . . . 820
  - composition of human, per 1,000 parts . . . 820
- Gay-Lussac tower . . . 182
  - law of (combination by volume) . . . 41
- Gelatin . . . 802
  - and chondrin, ultimate composition of . . . 802
- Gerhardt's base . . . 513
- "Gerhardt's base," chloride of . . . 513
- German dried yeast . . . 581
- German silver . . . 420, 429, 456
- Geysers . . . 223, 241
- Gibbsite . . . 438
- Gilding . . . 507
- Glance, cobalt . . . 495
- Glass . . . 363, 499
  - varieties of . . . 363
  - enamelling, coloring, painting, etc. . . . 364
  - action of fluorine on . . . 86
  - devitrification of . . . 363, 364
  - composition of various kinds of . . . 363
  - potash . . . 363
  - soda . . . 363
  - window . . . 363
  - soluble . . . 362
  - plate . . . 363
  - crown . . . 363
  - gall . . . 363
- Glauberite . . . 338, 379
- Glauber's salts . . . 356
- Glazing, salt . . . 446
- Globulin . . . 795, 811
- Glover's Tower . . . 182
- Glonoin . . . 677
- Glucinum (see Beryllium) . . . 447
- Glucosan . . . 684
- Glucose . . . 680, 684
  - left-handed . . . 685
- Glucoses, The . . . 684

PAGE
Glucosides, The . . . 686
Glue . . . 803
  marine . . . 655
Glycerin . . . 579, 657, 675, 737
  reactions of . . . 690
  series . . . 675
  soap . . . 735
Glycerides, The . . . 698, 705, 706, 734
Glycerol . . . 675
Glycocin . . . 703, 823
Glycocol . . . 703, 802
Glycogen or animal starch . . . 688
Glycol . . . 657, 741
  amylene . . . 672
  butylene . . . 672
  ethylene . . . 672
  hexylene . . . 672
  octylene . . . 672
  propylene . . . 672
Glycols, The . . . 632, 672
  aromatic . . . 674
  polyethylenic . . . 674
Glycyrrhizin . . . 686
Glyoxal . . . 674, 747
Gneiss . . . 443
Gold . . . 505
  history, natural history, extraction, properties, uses . . . 505, 506
  coinage . . . 506
  compounds of (*see under* Auric *and* Aurous) . . . 506
  standard . . . 506
  transparency of . . . 281
  reactions of the compounds of . 508
  fulminating . . . 508
  protochloride of . . . 507
  peroxide or sesquioxide of . . 507
  suboxide of . . . 507
  terchloride of . . . 507
Golden hair dye . . . 249
Goulard water . . . 703
Graham's sulphuric acid . . . 183
  diffusiometer and law of diffusion . . . 230
Grains, to convert into grammes . 843
Grammes, to reduce to grains . . 842
Granite . . . 443
Granulation of gunpowder . . . 349
Grape sugar . . . 684
Graphic or graphitic acid . . 199, 203
Graphite . . . 199
"Grass bleaching" . . . 590
Gravitation, definition of . . . 1
Gravitation modifies chemical action . . . 4
  elective or molecular . . . 1
Green salt of Magnus . . . 513
Green vitriol . . . 409
Greenockite . . . 468
Greenstone . . . 443
Grey antimony ore . . . 488
Grey powder . . . 539
Gros' chloride . . . 513
Grossularia . . . 335
Grotto del Cane . . . 212

PAGE
Grough . . . 321
Grove's battery . . . 511
Guaiacum resin . . . 653
Guanadine . . . 776
Guanine . . . 776
Guano . . . 828
Guignet's green . . . 414
Gum benzoin . . . 713
Gum, British or artificial . . . 689
  reactions of . . . 690
  resins . . . 654
Gums . . . 688
Gun-cotton . . . 790
  preparation, constitution, properties, 790, 791 ; decomposition . . . 349, 350
Gun-metal . . . 480
Gunpowder, 349 ; composition, properties . . .
  theory of explosions arising from 350
Gutta percha . . . 655
Gypsum . . . 171, 379, 383
  burnt . . . 383

H.

Hæmatein . . . 784
Hæmatin . . . 813
  chloride . . . 813
Hæmatite, brown . . . 399
  red . . . 399, 406
Hæmato-crystallin . . . 812
Hæmato-globulin . . . 812
Hæmatoidin . . . 813
Hæmatosin . . . 813
Hæmatoxylin . . . 784
Hæmin crystals . . . 812, 813
Hæmocyanin . . . 453
Hæmoglobin . . . 82, 399, 798
  preparation, properties . . . 812
Hair . . . 803
  dyes . . . 525, 537
Halogens, or haloid elements . . . 86
  generalisation on the . . . 113
Haloid acids, action of, on organic matters . . . 599
  elements . . . 86
  —action of the, on the metals . 285
  — — on organic bodies . . . 600
  ethers . . . 741
  salts . . . 300
  —double . . . 337
Haloids, general review of the compounds of hydrogen and the . 258
  compounds of the, with nitrogen 145
  as disinfectants . . . 589
Hardness of water . . . 247
Harrogate water . . . 171
Hartshorn, spirit of . . . 259, 596
Hausmannite . . . 391, 393
Heat modifies chemical action . . 14
  atomic . . . 46, 283
  molecular . . . 47

PAGE
Heat—*continued.*
  specific 45, 283
  unit of 45
  produced by the combustion of various substances 84
Heat and cold as natural disinfectants 588
Heated (super-) water 241
Heavy oil 595
  spar 171
Hepar sulphuris 346
Hepatic air 266
Heptads 51
Heptane 624
Heptylene 630
Herapathite 769
Hesperidene 651
Heterogeneous affinity 1
Hexads 51
Hexagonal system 66
Hexane 624
Hexdecane 624
Hexylene 630
Hippurates, The 714
Hoffmann's test for arsenic . . . 497
Hoffmann's violet 758
Homberg's phosphorus 149
  pyrophorus 442
Homogeneity 2
Homologous Series 621
Homoquinine 772
Honey stone 725
Hops, use of, in beer 586
Horn 596
Horn-lead 88, 526
Horn-mercury 88
Horn-quicksilver 542
Horn-silver 88, 530, 534
Houzeau's ozonometer 76
Humboldtite or iron resin . . . 410
Humus 590
Hyacinth 449
"Hydr" or "Hydro," the prefix . 30
Hydrargillite 438
Hydrargyrum 538
Hydrates, water unites with bases to form 244
"Hyd c̄ Cret" 538
Hydric bromide 253
  chloride 250
  dioxide (hydric peroxide) . . . 248
  fluoride 256
  hypochlorite 97
  iodide 255
  perchlorate 101
  peroxide 13, 248
  —synonyms, history, preparation, properties, 248; tests, 249; uses 250
  —a powerful oxidizing agent . 249
  persulphide 269
  phosphate 163
  phosphite 160
Hydrides, The 285, 311
Hydrocarbons, The 621, 623

PAGE
Hydrochloric acid 251
  —synonyms, history, natural history, 250; preparation, 250, 358; properties, 251.
  (solution) 251
  —preparation, properties . . . 251
  absorption co-efficient of . . . 242
  heat developed in formation of 16
  impurities of 252
  preparation of pure 253
  action on the metals of . . . 286
  table showing the percentage quantities of, and of hydrochloric acid gas contained in aqueous solutions of different specific gravities 837
Hydrogen 227
  absorption co-efficient of . . . 242
  absorption of, by carbon . . . 204
  weight of 229
  synonyms, history, natural history, 227; preparation, 228; properties 229
  compounds with carbon . 270, 277
  —with the haloid elements . . 250
  — — review of 258
  —with nitrogen 258
  —with oxygen 233
  —with phosphorus 263
  —with silicon 278
  —with sulphur 266
  estimation of the hydrogen and carbon in a body containing nitrogen 564
  experimental determination of the carbon, hydrogen and oxygen, of an organic compound not containing nitrogen . . 563
  —nascent, on organic bodies . . 602
  liquefaction and solidification of 229
  molecule 34
  pyrophosphate 162
  bicarburet of 638
  methane, or light carburetted . 271
  ethylene, or heavy carburetted . 272
  chloride of 250
  peroxide of (hydric peroxide) . 248
  —heat developed in the formation of 16
  gaseous phosphoretted 263
  —synonyms, natural history, preparation, 263; properties . 264
  —produced during fermentation 579
  liquid phosphoretted 265
  solid phosphoretted 265
  selenetted (seleniuretted) . . . 270
  sulphuretted 266
  —synonyms, history, natural history, preparation, 266; properties, 267; uses, tests . . 269
  persulphuretted 269
  siliciuretted 278
  telluretted 370
Hydrogenium 231, 284

PAGE
Hydrogenous compounds, action of chlorine on 92
Hydrometer, specific gravities corresponding to degrees of Baumé's 840
  degrees on Twaddell's, and the corresponding specific gravities 841
Hydroquinone 675
Hydroselenic acid 270
Hydrosulphides, The 309, 337
Hydrosulphurous hydrosulphate 269
Hydrosulphyl 269
Hydroxides, The 284, 299
Hydroxyl 248
Hydroxylamine 263
Hydroxyl ethene 663
Hydroxylmethane 662
Hygrometers 123
Hyoscyamine 776
"Hyper," the prefix 30
"Hypo," the prefix 30
Hypoantimonates, The 491
Hypochlorites, The 328
Hypochlorous oxide 96
Hypomolybdous bromide 515
  chloride 515
  oxide 515
Hypopalladous oxide 471
  sulphide 471
Hyponitrites, The 325
Hypophosphites, The 160, 330
  definition, preparation, properties 330
  uses in medicine 331
Hypophosphoric acid 158
Hypsometric thermometers 237
Hyposulphates, The 189
Hyposulphites, The (*see* Thiosulphates).
Hypotungstous bromide 554
  chloride 554
  iodide 554
Hypovanadic chloride 504
  oxide 504
Hypovanadous chloride 504
  oxide 504
Hypoxanthin 776

I.

"Ic," the termination 29
Ice, absorption of heat by, in becoming water 236
Iceland spar 384
Ice-making apparatus (Carré's) 260
"Ide," the termination 28
Illuminating agents, air vitiated by 126
Imides, The 258, 760
Imidogen 258
Inches, to convert cubic, into cubic centimetres 843
  to convert, into millimetres 843

PAGE
India-rubber 655
  vulcanized 655
Indian ink 653
Indian yellow 784
Indican 686
Indifferent oxides 74
Indigo 755, 783
  preparation of 783
  blue 686
  copper 461
  white 785
Indium 434
  history, natural history; extraction; properties 434, 435
  reactions of compounds of 436
  atomic weight of 434
  alum 435
  chloride 435
  hydrate 435
  nitrate 435
  oxide 435
  sulphate 435
  sulphide 435
  sulphite 435, 436
  yellow oxide of 435
Ine" and "in," the terminations 28
Inflammable air or gas 227, 271
Ink, composition of 410, 737
  blue sympathetic 426
Inosite, or sugar of muscle 686, 801, 803
Intestinal juice 823
Inulin starch 687, 688
Iodates, The 325
Iodides, The 303
  definition, natural history, preparation, properties, 303; tests, estimation, uses 304
  oxy, The 296, 304
Iodine 105
  preparation, Wollaston's process 106
  —Emil Bechi's process 107
  —Stanford's process 107
  compounds with starch 109
  estimation of chlorine, bromine, and iodine in an organic body 567
  action of, on organic bodies 601
Iodoform 627, 628
Iodopropane 626
Ions 19
Ipecacuanha 772
Iridic anhydride 518
  chloride 518, 519
  dioxide 518
  hydrate 518
  iodide 518
  osmide 509
  sesquichloride 518
  sesquioxide 518
  sulphide 518
Iridium 517
  history, derivation, natural history, preparation; properties, 517, 518
  compounds of 518
  black 518

PAGE

- Iridium spongy . . . 518, 519
- Iridous chloride . . . 518
  - oxide . . . 518
  - sulphide . . . 518
- Iron . . . 398
  - history, natural history; preparation; impurities; properties . . . 328-404
  - compounds of (*see* Ferrous *and* Ferric) . . . 404
  - —with oxygen . . . 405
  - —with chlorine . . . 407
- Iron, calcination of . . . 399
  - puddling, of . . . 401
  - refining of . . . 401
  - roasting of . . . 399
  - smelting of . . . 400
  - welding of . . . 403
- Iron alum . . . 405, 410
  - bar . . . 402
  - cast, composition of . . . 401
  - dialyzed . . . 406
  - galvanized . . . 420
  - glance . . . 399
  - grey . . . 401
  - meteoric . . . 398
  - mottled . . . 401
  - ores . . . 399
  - passive state of . . . 404, 410
  - power of, to absorb gases . . . 284
  - pyrites . . . 171, 399, 408
  - rust . . . 403, 406
  - scales . . . 406
  - slag . . . 400, 410
  - specular . . . 406
  - stone (siliceous) . . . 399
  - tenacity of . . . 282
  - white . . . 401
  - wrought . . . 403
- Iron, black oxide of . . . 406
  - carbide of . . . 401
  - cold blast . . . 401
  - hot blast . . . 400
  - magnetic oxide of . . . 403, 404, 406
  - nitrides of . . . 404
  - oxychloride of . . . 407
  - oxy-salts of . . . 407
  - perchloride, sesquichloride or trichloride of . . . 407
  - per-salts of . . . 406
  - —reactions of . . . 411
  - persulphate or sesquisulphate of . . . 410
  - protocarbonate of . . . 410
  - protochloride of . . . 407
  - proto-salts of . . . 405
  - —reactions of . . . 410
  - protosulphate of . . . 409
  - protosulphide or sulphide of . . . 408
  - protoxide of . . . 405
  - red oxide of . . . 405
  - sesquioxide or peroxide of . . . 405
  - silicates of . . . 410
  - spathic ore . . . 410
  - vitriol . . . 409

PAGE

- Ironmould . . . 403
- Iron resin or Humboldtite . . . 410
- Isatin . . . 79, 93, 785
- Isinglass . . . 802
- Isoamylbenzene . . . 634
- Isoamyldimethylbenzene . . . 634
- Isoamylmethylbenzene . . . 634
- Isobutylbenzene . . . 634
- Isocyanides . . . 762
- Isologous series . . . 622
- Isomerism . . . 59
- Isomorphism . . . 61
- Isoparaffin . . . 626
- Isoprene . . . 655
- Isopropylbenzene . . . 634
- Isopropyldimethylbenzene . . . 634
- Isopropylmethylbenzene . . . 634
- "Ite" and "Ate," terminations . . . 29
- Ivory black . . . 199

J.

- Jalap resin . . . 653
- Jargonelle pear, artificial essence of . . . 703
- Jasper, amorphous variety of silica 223
- Jewellers' rouge . . . 405

K.

- Kakodyl . . . 764
  - chloride . . . 765
  - cyanide . . . 765
  - dioxide . . . 765
  - disulphide . . . 765
  - iodide . . . 765
  - oxide . . . 765
  - sulphide . . . 765
  - trichloride . . . 765
- Kalium . . . 340
- Kaolin, a white clay . . . 444, 446
- Kapnomor . . . 597
- Kelp, or varec, ash of sea-weed, 106, 344, 357
- Kerargyrite . . . 530, 534
- Kermes mineral . . . 493
- Ketone, dimethyl . . . 748, 749
  - methyl ethyl . . . 748
  - —isopropyl . . . 748
  - —propyl . . . 748
  - —butyl . . . 748, 749
  - —isoamyl . . . 748
  - diethyl . . . 748
  - dipropyl . . . 748
  - ethyl propyl . . . 748
- Ketones, the . . . 623, 748
  - constitution, 748; preparation, properties, and reactions . . . 749
  - distinction from aldehydes . . . 749
- Kieserite . . . 389
- King's yellow . . . 501

PAGE
Klumene . . . 274
Kobellite . . . 464
Kolbe's classification of alcohols . 658
Koumiss, fermented mare's milk . 586
Kreasote, coal tar . . . 670
  to distinguish carbolic acid from wood . . . 597
Kreatine . . . 776, 801
Kreatinine . . . 776, 801
Kryolite . . . 354
Kupfernickel . . . 495

L.

Labarraque's fluid . . . 589
Labradorite . . . 335, 443
Lac . . . 653
Lac dye . . . 653
Lacquer . . . 653
Lactamide . . . 709
Lactide . . . 709
Lactin or lactose . . . 579, 683
Lævoglucose . . . 685
Lævulosan . . . 685
Lævulose . . . 685
  natural history, preparations, properties . . . 685
Lagoons . . . 219
Lakes (pigments) . . . 439, 784
Lampblack . . . 199, 200
Lana philosophica . . . 420, 421
Lanarkite . . . 528
Lanthanum . . . 452
Lanthanous chloride . . . 452
  hydrate . . . 452
  oxide . . . 452
  nitrate . . . 452
  sulphate . . . 452
Lapis lazuli . . . 443
Laughing gas (nitrous oxide) . . 128
Laurite . . . 476
Lazulite . . . 442
Lead . . . 520
  history, natural history, preparation, impurities, purification 520-523
  action of air upon . . . 522
  —of water upon . . . 522
  —of waters containing silica upon . . . 522
  compounds of (*see* Plumbic *and* Plumbous salts) . . . 523
  —lead and oxygen . . . 521
  —of lead and sulphur . . . 527
  extraction of silver from . . . 521
  properties of . . . 521
  reaction of the salts of . . . 529
  acetate of . . . 528
  carbonate of . . . 528
  chlorosulphide of . . . 527
  chromate of . . . 416
  impurity of sulphuric acid . . 184
  oxychlorides of . . . 526

PAGE
Lead—*continued.*
  oxy-salts . . . 527
  protosulphide of . . . 527
  protoxide or monoxide of . . . 524
  puce or brown oxide of . . . 525
  pyrophoric . . . 5
  red ore of . . . 416
  shot . . . 496
  suboxide of . . . 524
  subsulphide of . . . 527
  sugar of . . . 703
  sulphochlorides of . . . 523
  uses . . . 523
Lead, brown oxide . . . 525
  hard . . . 521
  plaster . . . 733
  red . . . 525
  soft . . . 521
  vitriol . . . 528
  white, preparation of . . . 528
Leather . . . 736, 802
Leaven . . . 586
Leaves, coloring matter of . . . 399
Leblanc's process for manufacture of sodium carbonate . . . 357
Lecithin . . . 803
Legumin . . . 796
Lepidolite . . . 365, 366, 443
Leucine . . . 705, 802
Leucite . . . 340
Leucoline . . . 592
Leukon or silico-formic acid . 226, 279
Libavius, fuming liquor of . . . 482
Libethenite . . . 463
Lichen starch . . . 687, 688
Liebigite . . . 431
Light, influence of, on affinity . . 18
  action of, on nitric acid . . . 143
  —organic bodies . . . 588, 603
  —phosphorus . . . 154
Lignin . . . 789
Lignite . . . 205, 206
Lime, uses of . . . 381
  slaked . . . 381
  chloride of . . . 328, 385
  kilns . . . 211, 381
  milk of . . . 381
  air slaked . . . 381
  water . . . 381
  as a disinfectant . . . 589
Limestone . . . 379, 381, 384
Limonite . . . 399
Liquid anibar orientale . . . 640
Liquids, solubility in water of . . 241
  diffusion of . . . 240
  homogeneity in the case of . . 3
Liquor arsenicalis . . . 334
  sanguinis . . . 813
Litharge (plumbic oxide) . . . 524
Lithia . . . 365
Lithium . . . 308, 365
  history, natural history, preparation, properties, uses . . . 365
  compounds . . . 365
  —reactions of the . . . 366

PAGE

- Lithium—*continued.*
  - carbonate . . . 36
  - chloride . . . 365
  - dithionate . . . 365
  - fluoride . . . 365
  - hydrate . . . 365
  - iodide . . . 365
  - nitrate . . . 365
  - oxide . . . 365
  - perchlorate . . . 365
  - phosphate . . . 365
  - spectrum of . . . 366
  - sulphate . . . 365
- Litmus . . . 783, 785
- Live lime . . . 381
- Liver of sulphur . . . 346
- Loadstone . . . 399, 406
- Loam . . . 444
- Logwood . . . 784
- Lucifer matches . . . 157
- Lugol's solution . . . 108
- Luminous paints . . . 377, 383
- Lunar caustic . . . 536
- Lupuline, use of, in beer . . . 586
- Lustre, metallic . . . 281
- Luteo-cobaltic chloride . . . 427
- Luteoline . . . 784
- Lutidine . . . 754
- Lymph and chyle . . . 816
  - percentage composition of . . . 817

M.

- Madder, preparation of . . . 783
- Magenta . . . 757, 758
- Magistral . . . 530
- Magnesia (magnesic oxide) . . . 388
  - alba . . . 390
  - calcined . . . 388
  - usta . . . 388
- Magnesian limestone . . . 386
- Magnesite . . . 390
- Magnesium . . . 386
  - history, natural history, preparation, properties, uses . . . 386, 387
  - compounds of . . . 388
- Magnesium aluminate . . . 439
  - ammonium arsenate . . . 388
  - —carbonate . . . 390
  - —chloride . . . 380
  - —phosphate . . . 388, 390
  - arsenate . . . 332, 388
  - aurate . . . 507
  - borate . . . 336, 338
  - boride . . . 276, 279, 388
  - bromide . . . 388, 389
  - calcic carbonate . . . 390
  - carbonate . . . 388, 390
  - chloride . . . 388, 389
  - fluoride . . . 388, 389
  - hydrate . . . 388
  - iodide . . . 388, 389

PAGE

- Magnesium—*continued.*
  - nitrate . . . 388
  - nitride . . . 310, 388, 389
  - oxide . . . 388
  - oxychlorides . . . 389
  - phosphate . . . 388, 390
  - potassic carbonate . . . 390
  - —chloride . . . 389
  - —phosphate . . . 390
  - —sulphate . . . 390
  - —silicide . . . 388
  - pyrophosphate . . . 388, 390
  - silicates . . . 335, 388, 390
  - sodic fluoride . . . 389
  - —phosphate . . . 390
  - sulphate . . . 388, 389
  - sulphide . . . 388, 389
  - sulphydrate . . . 388, 389
- Magnesium light . . . 387
- Magnetics and diamagnetics . . . 284
- Magnetic oxide of iron . . . 399
  - properties of metals . . . 284
  - pyrites . . . 409
- Magnetite . . . 406
- Magnus's, green salt of . . . 513
- Malachite . . . 453, 463
- Malamide . . . 761
- Malimide (?) . . . 761
- Malleability of metals . . . 282
- Malting . . . 585
- Manganates, The . . . 316, 395
  - definition, preparation, properties, uses . . . 316
- Manganese . . . 391
  - history, natural history, preparation, properties, uses . . . 391
  - compounds of . . . 392
  - —reaction of the . . . 398
  - alum . . . 392, 398
  - aluminium alum . . . 398
  - blende . . . 391, 397
  - binoxide, peroxide or black oxide of . . . 394
  - red oxide of . . . 392, 393
  - sequioxide of . . . 393
  - spar . . . 391, 397
- Manganic acid . . . 392, 395
  - anhydride . . . 392
  - chloride . . . 392, 397
  - hydrate . . . 393
  - oxide (sesquioxide) . . . 392
  - oxides . . . 391, 392, 393, 394
  - oxychloride . . . 392, 397
  - perchloride . . . 392
  - perfluoride . . . 392
  - peroxide . . . 392
  - —regeneration of . . . 395
  - sesquioxide . . . 392
  - sulphate . . . 392, 398
  - sulphide . . . 392, 397
  - tetrachloride . . . 397
- Manganite . . . 393
- Manganites, The . . . 394
- Manganosite . . . 393
- Manganous bromide . . . 392

PAGE

Manganous—*continued.*
  carbonate 391, 392, 397
  chloride 392, 394, 396
  chromite 413
  dithionate 189, 320, 392
  fluoride 392
  hydrate 392, 393
  iodide 392
  nitrate 392, 398
  oxide 392, 393
  silicate 391, 392
  sulphate 392, 394, 397
  sulphide 392, 397
Mannite 579, 580, 657, 678
  preparation, properties 678
Marble 379, 381, 384
  artificial 384
Marcasite 408
Margarin 734
Marine acid 250
  glue 655
Marl 444
Mars, crocus of 405
Marsh gas 271
  action of chlorine on. . . 93, 629
  —series or paraffins 624
  —type 48, 58
Marsh's test for arsenic . . 497, 503
Mason's wet and dry bulb thermometers 123
Mass or quantity, influence of, on affinity 11
Massicot (plumbic oxide) . 524, 525
Masson's patent 587
Mastich 653
Mat (copper coarse metal) . . . 454
Matches, safety 157
Mauve (aniline purple) . . 757, 758
Maximum work, law of 17
Meadow bleaching 77
Meadowsweet 602
Measures (*see* Metric System).
Mechanical and chemical mixtures 2
Mechanical force may modify chemical action 12
Meerschaum 390
Melampyrite 679
Melene 630
Melissine 630, 657
Melitose 680, 683
Melizitose 680, 684
Mellone 612
Mellonides, The 612
Mendeleeff's law of periodicity . 52
Mendipite 526
Menthene 651
Mephitic air 210
Mercaptans or thio-alcohols, 661, 679, 741
Mercuramine 542
Mercuric ammonium chloride 540, 545
  bromide 540
  carbonate 541
  chloride 540
  chromate 542

PAGE

Mercuric—*continued.*
  cyanide 607
  ethide 767
  fluoride 540
  fulminate 608, 612
  hydrate 542
  iodide 540, 546
  mellonide 612
  mercaptide 679
  methide 767
  nitrate 541
  nitride 310, 541, 542, 548
  oxide 14, 540, 541
  oxy-chlorides 544
  phosphate 541
  sulphate 541, 548
  sulphide 540, 547
  sulphocyanate 612
Mercurous bromate 325, 540
  bromide 540
  carbonate 540
  chlorate 540
  chloride 540, 542
  —dissociation of 543
  fluoride 540
  iodide 540, 546
  nitrate 540, 549
  oxide 540, 548
  perchlorate 327, 540
  phosphate 549
  sulphate 540, 548
  sulphide 540, 547
Mercury 538
  history, natural history, extraction, properties, uses . . 538-540
  action of air and water on . . 538
  color of the film of 538
  reactions of the salts of . . . 549
  compounds of 540
  —chlorine with 542
  —iodine with 546
  —sulphur with 547
  vapor density of 44, 538
  biniodide of 546
  black or grey oxide of 541
  chloride, bichloride, or perchloride of 544
  fulminating 542
  green iodide of 546
  Hahnemann's soluble 549
  nitric oxide of 541
  nitride of 548
  oxy-salts of 548
  protonitrate of 548
  red iodide of 546
  red oxide of 541
  subchloride or protochloride of . 542
  subsulphide of 547
Mesitylene 634, 635
Meso paraffin 626
"Meta," the prefix 30
Metaldehyde 745
Metallic butters 301
  oils 301
Metalloids, The 67

PAGE

- Metals . . . 280
  - absorption of gases by . . . 284
  - alloys of the . . . 289
  - brittleness of the . . . 282
  - chemical properties of the . . . 284
  - classification of the . . . 288
  - conductivity (electrical) of, 283, 291
  - crystalline forms of the . . . 281
  - derivation, definition, order of discovery, natural history . . . 280
  - ductility of the . . . 282
  - elasticity of the . . . 281, 290
  - expansion by heat of the . . . 283
  - fusibility of the . . . 283, 296
  - general remarks on the . . . 339
  - hardness of the . . . 281, 290
  - lustre of the . . . 281
  - magnetic properties of the . . . 284
  - malleability of the . . . 282
  - opacity of the . . . 281
  - property of transmitting light . 281
  - sensible and physical properties . . . 281
  - sonorousness of the . . . 281, 290
  - specific gravity of the . . . 282, 290
  - tenacity of the . . . 282, 290
  - texture of the . . . 281
  - volatility of the . . . 283
  - welding of the . . . 283
- Metals, action of acids on the . . . 286
  - —of boron on the . . . 285
  - —of carbon on the . . . 285
  - —of haloid elements on the . . . 285
  - —of hydrogen on the . . . 285
  - —of nitrogen on the . . . 285
  - —of oxygen on the . . . 284
  - —of phosphorus on the . . . 285
  - —of selenium on the . . . 285
  - —of silicon on the . . . 285
  - —of tellurium on the . . . 285
  - —of water on the . . . 286
- Metamerism . . . 59, 60
- Metantimonates, The . . . 491
- Metapectin . . . 690
- Metaphosphates, The . 162, 165, 330
- Metastannates, The . . . 481
- Metaterebenthene . . . 649
- Metatungstates, The . . . 554
- Metaxylene . . . 634
- Meteoric iron . . . 227
  - (Lenarto) . . . 231
- Meteorites, gases in . . . 227, 271
  - nickel in . . . 429
- Methæmoglobin . . . 813
- Methæmatin . . . 813
- Methane or light carburetted hydrogen . . . 271, 624, 629
  - synonyms, history, natural history, preparation, 271; properties, 229.
  - decomposition by heat of . . . 15
- Methenyl chloride . . . 629
- Methyl . . . 622
  - carbinol . . . 663
  - cyanide . . . 628, 629, 695

PAGE

- Methyl—*continued.*
  - diethyl carbinol . . . 659
  - ethyl . . . 624
  - —ketone . . . 666
  - ethylamine . . . 753
  - ethyl-phenylamine . . . 753
  - glycocin . . . 703
- Methylamine . . . 662, 752
- Methylbenzene . . . 634, 639
- Methylene chloride . . . 628
- Methylia . . . 776
- Methylic acetate . . . 703
  - alcohol . . . 598
  - chloride . . . 628
  - —dichlorinated . . . 629
  - hydride . . . 271, 629
  - naphthalene . . . 640
  - salicylate . . . 662
- Metric system as a measure of length . . . 62
  - —as a measure of surface . . . 62
  - —as a measure of capacity . . . 62
  - —as a measure of weight . . . 63
- Meyer (Lothar) on periodicity . . 54
- Mezereon resin . . . 653
- Mica . . . 87, 443
- Microcosmic salt . . . 164, 329, 372
- Milk . . . 817
- Milk of cows . . . 698
  - composition per 100 parts of human compared with that of the cow . . . 818
- Milk of lime . . . 381
- Milk sugar . . . 579
- Millerite . . . 430
- Millimetres, to reduce, to inches . 842
- Millon's reaction with the proteids . . . 798
- Mineral chamelion . . . 396
- Mineral green . . . 463
  - yellow . . . 526
- Mineral waters . . . 246
- Minium . . . 525
- Miscible naphtha . . . 598
- Miscibility . . . 7, 241
- Mispeckel . . . 495
- Mixture, chemical and mechanical 2
- Moirée métallique . . . 479
- Moisture in air (*See* Gaseous vapours).
- Molecular formulæ . . . 572
  - gravitation . . . 1
  - heat, law of . . . 47
  - volumes . . . 41, 45
  - —of gases . . . 41
  - —of solids . . . 44
  - —of liquids . . . 44
  - – calculation of . . . 43
  - weights . . . 34, 43
  - —of elements . . . 44
  - —and boiling points . . . 47
- Molecule, compound and elementary . . . 33
  - saturated and unsaturated . . 622
- Molybdates, The . . . 317, 516

PAGE
Molybdenum 514
  compounds of 515
  —tests for 517
  natural history, preparation, properties 514, 515
Molybdic anhydride 515
  chloride 515
  oxytetrachloride 515
  oxide 515
  pentachloride 515, 516
  persulphide 515, 517
  sulphide 515, 517
  tetrasulphide 515
Molybdous chlorides . . . 515, 516
  hydrate 515
  oxide 515
  sulphide 515
"Mon" or "mono," "deut," etc., the prefixes 29
Monads 50
Monadelphic double type 560
Monamides, primary, secondary, and tertiary 760
Monamines 750
Monazite 450
Mond's process 359
Monobromobenzene 639
Monochlorobenzene 639
Monochloromethane 628
Monohydrogen phosphate . . . 161
Monoclinic system 66
Moor's test for sugar 685
Morindin 784
Mordant, alum as a 439
Morphine 60, 773
  tests for 781
Mortar 381
  hydraulic 382
Mosaic gold 483
Mottramite 504
Mucin 833
Mucoid sugar 680
Mucous or viscous fermentation . 580
Mucus 833
Mudie's disinfectant 589
Mulberry calculus 719, 832
Multiple proportions, law of . . 35
Mundic 408
Murexide 828, 829
Muride 102
Muscle 795
  sugar of 686, 801, 803
Mustard, essence of 172
  oil of 581, 686
Mustard oils 613
Mycoderma aceti 580
Mycose 680, 684
Myosin 795
Myricin 734
Myrosin 581

N.

Names of bodies 27
Naphtha coal 595

PAGE
Naphtha, wood 597
Naphthalene 592, 641
  occurrence, preparation, properties, etc. 641
  series 640
Naphthaladine. 753
Naphthoquinone 681
Naphtoic series, acids of the . . 717
Narceine 773
Narcotine 773
  tests for 781
Nascent matter, action of. . . . 11
Neodymium 450
Neoparaffin 626
Nerve tissue 803
Nessler's solution 373
Nettles, acid of 700
Neutralisation 546
Nickel 428
  history, natural history, preparation, properties, uses . 428, 429
  alloys of 429
  compounds of 429
  glance 428, 452, 495
  ores of 428
  plating. 429
  protoxide of 430
  reactions of the salts of . . . 431
Nickelic hydrate 429, 430
  oxide 429, 430
  sulphide 429, 430
Nickelous arsenate 429
  bromide 429, 430
  carbonate 429
  chloride 429, 430
  fluoride 429, 430
  hydrate 430
  iodide 429, 430
  nitrate. 429, 431
  nitrite 431
  oxide 429, 430
  phosphate. 419
  silicate. 429
  sulphate 429, 430
  sulphide 429, 430
Nicotine 770
Nil album (zinc oxide) 420
Niobates, The 505
Niobium 504
  compounds of 505
Nitraniline 757
Nitrates, The 320
  definition, synonyms, natural history, 320; theories of nitrification, 321; purification of nitre, 321; preparation, properties, 322; tests, uses, 323.
  salts allied to the . . . . . .
Nitre, converted 348
Nitre or saltpetre 140, 348
  cubical 320
  form of, requisite for gunpowder 349
  plantations or heaps 321
  prismatic 320
  purification of (refining) . . . 321

PAGE
Nitre—*continued.*
  sweet spirits of 742
  testing 323
Nitric acid (*see* Acid, nitric).
  action of, on the metals 286
  action of, on organic matter 599
Nitric dioxychloride (nitrylic chloride). 148
  dioxy-tetrachloride (chloro-nitric gas) 148
Nitric oxide. 131
  synonyms, preparation, properties 131
  oxy-dichloride (chloro-nitric gas) 148
  peroxide 128, 132, 134
  —synonyms, 134; history, preparation, properties, 135.
  trioxide 133
Nitrides, The 117, 285, 310
Nitrification 81
Nitriles, The 761
Nitrites, The 323
  formation of. 323
Nitrobenzene 639
Nitro-ethane 628
Nitrogen 115
  synonyms, 115; history, 115; natural history, 115; preparation, 116; properties, 117; tests, 117; uses, 118.
  absorption by carbon. 204
  —coefficient of 242
  compounds (*see below*).
  —with the haloids 145
  —with hydrogen 258
  —with oxygen 128
  estimation of 120, 565
  —of the hydrogen and carbon in a body containing 564
  general remarks on the oxides of nitrogen 138
  a grouping element for nitrogenized bodies 560
  present in various animal substances 116
  quantity of, in the air 120
  recognition of, in organic bodies 565
Nitrogen, binoxide (deutoxide) of 131
  chloride of 145
  dioxide 131
  iodide of 146
  monoxide 128
  oxides of, general remarks on the 138
  pentoxide 139
  protoxide 128
  tetroxide 134
  trioxide 133
Nitro-cellulin 790
Nitro-glycerine 677
Nitro-methane 628
Nitro-naphthalene 641
Nitro-paraffins 790
Nitro-prussides 617
  tests for 620

PAGE
Nitro-sucrose 682
Nitrosyl 131
  bromide 147
  chloride (nitrous oxychloride) 139, 147
  sulphate 147
Nitrotrichloromethane 630
Nitrous air 131
Nitrous bromide 146
  chloride 145
  hydrobiniodide 146
  iodide 146
  —(nitric peroxide) 134
  oxide 128, 133
  —synonyms, history, and preparation, 128; properties, 129; uses, 130.
  —absorption by carbon of 204
  —absorption co-efficient of 242
  oxybromide 147
  oxychloride 147
  —synonyms, preparation, properties 147
Nitrous sulphuric acid 182
Nitroxyl chloride 148
Nitryl 134
Nitrylic chloride 148
  —synonyms, preparation, properties 148
Nobel's blasting oil 677
Nomenclature 27
Nonane 624
Nonene 630
Nonylene 630
Nordhausen sulphuric acid 181, 409
Norwegium 452
Nut galls 737

O.

Oak bark 736
Obsidian or volcanic glass 443
Occlusion of hydrogen 231, 284
  —of carbonic oxide by steel 402
Ochre (red) 399, 444
  (yellow) 399
  (Wolfram) 553
Octads 51
Octane 624
Octene 630
Octylene 630
Odds or perissads 52
Odors, power of carbon for absorbing 204
Odling on ozone 75
Oil, bitter almond 651
  bone 801
  cocoa nut 698
  earth nut 698
  fusel 698
  paraffin 647
  rock or petroleum 647
  rue 698
  tree 698

PAGE

Oil of camphor 651
  of sulphur 181
  of turpentine and its allies . . 648
  of vitriol 181
Oil wells, gases from 227
Oils and fats 731
Oils, cause of certain oils drying . 590
Oils, essential or volatile . . 650, 651
  preparation, properties, 650; table of essential oils . . . 651
  volatile, as disinfectants, 589, 650, 734
  drying, table of 733
  fish, table of 733
  fixed 731
  —action of heat on the, and solubility of 732
  — —air (rancidity) 732
  —list of fatty bodies 733
  —non-saponifiable 734
  —saponifiable 732
  —tabulated list of fats and oils . 733
  metallic 301
  non-drying, table of 733
Okenite 335
Olefiant gas 272
Olefiant gas series of hydrocarbons 630
  decomposition by heat of . . . 15
Olefines, the 630
  preparation, properties of the . 630
Olein 676, 734
Oleo-resins 654
Olive oil 733
Onyx, an amorphous variety of silica 223
Oolite 384
Opal, an amorphous variety of silica 221, 223
Ophite 335
Opium, alkaloids of 773
Ooze 737
Orange chrome 416
Orceine, a red coloring matter 675, 783
Orcin 657, 675
Orcins, The 674
Organic analysis 560
Organic bodies, ultimate analysis of 561
  proximate analysis of 576
  natural and artificial changes of 578
  types of 559
  action of acids on 598
  —alkaline hydrates on 600
  —alkaline carbonates on . . . 600
  —haloid elements on 600
  —heat on 591
  —light and electricity on . . . 603
  —nascent oxygen on 601
  —nascent hydrogen on 602
Organic chemistry 556
  definitions of 556
Organic compound and organised body, distinction between . . 556
Organic matters in the air . . . 126

PAGE

Organisms, the part they play in fermentation 578
Organo-boron compounds . . . 766
Organo-metallic compounds. . . 765
Organo-silicon compounds . . . 766
Orpiment 495, 501
Orthophosphates 166, 329
Orthoclase 340, 443
Osmates, The 476
Osmic acid 474
  chlorides 475
  oxides 475
  sulphide 475
Osmium 474
  atomic weight of 474
  history, natural history, extraction, properties, 474.
  compounds of 475
  —reactions of the 476
Osmiridium 474, 517
Osmosis 230
Osmous chloride 475
  oxide 475
  sulphite 476
Ossein 800
Osteolite 150, 379, 385
"Ous," the termination 28
Ov-albumen 795
Oxalates 720
Oxalic ether 720
Oxaluria, use of oxygen in . . . 85
Oxamide 668, 760
Oxides, The. 284, 296
  —preparation of the 296
  —properties of the 298
  —table of the 297
  —varieties of the 296
  acid 297
  basic 296
  fusibility of the 298
  neutral 297
  action of acids on the 299
  —chlorine on the 299
  —sulphur on the 299
  —water on the 298
  indifferent 74
Oxidising bodies, action of, on sugar 682
Oxy-benzene 670
Oxychloride, definition of term . 290
Oxygen 68
  synonyms, 68; history, 68; natural history, 69; preparation, 69; properties, 73; allotropic oxygen or ozone, 75; uses of oxygen, 81.
  absorption by carbon of . . . 204
  —by molten metals of 76
  —co-efficient of 242
  action of, on the non-metals . . 74
  —on the metals 74
  —nascent, action on organic bodies 601
  — —on alkaloids 11
  amount needed for respiration by an average man 82

PAGE

Oxygen—*continued.*
  Brin (frères), process of, for the preparation of 70
  compressed, physiological action of 73
  estimation of 75, 120, 563
  experimental determination of, in an organic compound not containing nitrogen 563
  its use in combustion 84
  in the air 82, 120
  liquefaction of 73
  use of, in medicine 85
Oxygenated muriatic acid gas . . 88
Oxygenated water 248
Oxyhæmoglobin 82
Oxyiodide, definition of the term . 296
Oxyphenol 657, 675
Oxysalts 311
Oyster shells, composition of . . 379
Ozokerit 647
Ozone 75, 590
  history, 75 ; nature, 75 ; preparation, 76 ; properties, 78 ; tests, 79 ; quantitative determination, 80.
  faculty of phosphorus for evolving, in damp air 77
  presence of, in the air 122
Ozonizers 76, 79

P.

Packfong 429
Painting on glass 364
Palladic chloride 471, 472
  oxide 471, 472
  sulphide 471, 473
Palladium 470
  history, natural history, extraction from platinum ores, from gold ores ; properties. . 470, 471
  absorption of hydrogen by. 231, 470
  action on ethylene of 471
  alloys of 471
  chloride of 472
  compounds of 471
  —reactions of the 473
  hydride 311
  spongy. 470
  suboxide of 472
  subsulphide of 473
Palladous chloride 471
  cyanide 471, 472, 607
  hydride 471, 472
  iodide 471, 472
  nitrate 471
  oxides 471
  sulphate 471
  sulphides 471, 473
Palm oil 705
Palmitates, The 705
Palmitin 676, 734

PAGE

Pancreatic fluid 821
  composition of, per 1,000 parts . 821
Pancreatin 819, 822
Papaverine 773
Papin's digester 801
"Para," the prefix 30
Paracyanogen 604
Paraffin 647
  oil 647
Paraffins, The 272, 624
  preparation of the 626
  general properties, the 627
Paraglobulin 795, 808, 814
Paraldehyde 745, 771
Paramylon 687, 688
Paranaphthalene 643
Paraniline 754
Paranthracene. 644
Parapectin 690
Paraxylene 634
Parchment, vegetable 790
Paris yellow 526
Parke's process for extracting silver 521
Parvoline 754
Passive iron. 404, 410
Pattinson's process for extraction of silver 521
Pattinson's white lead oxychloride 526
Pea iron ore. 399
Pear, essence of jargonelle . . . 742
Pearlash 343, 348
Pearl hardener (calcic sulphate) . 384
Pearl white 467
Peat 205
Pectin. 689, 793
Pectose 689, 792
Penicillium glaucum . . . 580, 581
Pentachlorobenzene. 639
Pentachlorophenol 671
Pentadecane 624
Pentad elements 51
Pentane 624
Pentathionates, The. 320
Pentene 630
Pepsin 819, 820
Peptones 797, 820
"Per," the prefix 29
Perchlorates, The 327
Perchloric oxide 99
Periclase 388
Pericline 443
Peridote 335
Periodates, The 327
Periodicity, Mendeleeff's law of . 52
  table 53
Perissads, or odds 52
Permanent white. 377
Permanganates, The . . . 316, 395
Pernitric oxide 134
Peroxide of chlorine 99
  of hydrogen (hydric peroxide) . 248
  of nitrogen 134
Perruthenates, The 477
Persulphide of hydrogen 269

PAGE
Persulphocyanogen 612
Persulphuretted hydrogen 269
Peruranates, The 433
Petatite 365, 443
Petroleum 647
 oil 647
 spirit 647
Pewter 480, 488
Pharaoh's serpents 613
Phenacite 335, 447
Phenanthrene 592, 645
Phenates, The 672
Phenol (*see* Acid, carbolic).
Phenols, The 668
Phenoquinone 672
Phenose 639
Phenylamine 755
Phenylbutylene 640
Phenylethylene 640
Phenylia 755
Phenylic hydride 638
Phenyl isocyanide 762
Philosopher's wool (zinc oxide) 420, 421
Phlogisticated vitriolic acid 175
Phlogiston and phlogistic theory 69, 115, 149
 as a synonym of hydrogen 227
Phlorizin 686
Phloroglucin 677
Phloroglucol 677
Phlorol 669
Phosgene gas 18, 36, 216
Phospham 169
Phosphamine 263
Phosphamimide 170
Phosphates, The 329
 Fleitmann's and Henneberg's 330
Phosphides, The 310
Phosphine 263
Phosphines, The 763
Phosphites, The 331
 definition; properties, tests 331
Phosphomolybdates, The 516
Phosphoric bromide 169
 chloride 169
 iodide 169
Phosphoretted hydrogen, gaseous 263
 —liquid 265
 —solid 265
Phosphoric chloride 167, 602
 —synonyms, preparation, properties 168
 —abnormal vapor density of 45, 168
 dodecasulphide 193
 fluoride 169
 hydrobromide 264
 hydro-iodide 264
 iodide 265
 oxide, a dehydrating agent 602
 oxytriamide 170
 oxytrichloride 168
 sulphide 193
 sulphobromide 194

PAGE
Phosphoric—*continued.*
 sulphotrichloride 193
 —synonym, preparation, properties 193, 194
Phosphorite 379, 385
Phosphorous acid. 158
 anhydride 158
Phosphorus 149
 history, 149; natural history, 150; preparation, 151; varieties, 152; properties, 152; solubility, 154; tests, 157; uses, 157.
 action of ammonia on compounds of 169
 compounds with oxygen 158
 —with the haloids 167
 —with hydrogen 263-265
 —with sulphur. 193
 estimation of, in an organic body 567
 general remarks on the acids of the oxides of phosphorus 164
 proportion of, per cent. present in various animal tissues 150
 —in various vegetable tissues 150
 —in which certain gases stop the slow combustion of 155
 quantities of vapor required to check the luminosity of, in air at elevated temperatures 155
 solubility in various liquids 154
 amorphous 152
 black 152
 Canton's 383
 physiological action of 152, 157
 red 152
 vapor density of 44
 white 152
Phosphorus, iodides of 169
 bromide 169
 bromochloride 169
 chloride 167
 iodide 169
 oxide (phosphorous anhydride) 160
 oxychloride of 168
 pentachloride or perchloride of 167
 sesquisulphide 193
 suboxide of 158
 sulphides 193
 sulphochloride of 193
 sulphobromochloride 169
 trichloride or terchloride of 167
 trihydride 263
 trioxide (phosphorous anhydride) 160
 Baldwin's (calcic nitrate) 149
 Bolognian (baric sulphate) 149
 Homberg's (fused calcic chloride). 149
Phosphoryl chloride or trichloride 168, 169
 chlorobromide 169
 nitrate 170
Phosphotungstates, The 555

PAGE
Photography 535
Phyllocyanine 785, 786
Phylloxanthin 784, 786
Physiological properties of bodies influenced by affinity. . . . 3
Physostigmine 776
Picoline 592, 754
Pictet's liquefaction of oxygen and hydrogen 73, 229
Pigments in urine 830
Pil. hydrargyri 539
Pitchblende 431
Pimple 455
Pink salt 483
Piperidine 754
Piperine 775
Pit gas 271
Pitch 596, 598
Plants, life of 85, 198, 791
  manganese in 391
Plasma 813
Plaster of Paris 383
Platino diammonic chloride . . . 513
  tetrammonic chloride 513
Platino nitrites, The 514
Platinates, The 512
Platinamine 513
Platinic acid 512
  ammonic chloride 509
  bromide 511
  chloride 511
  hydrate 511
  iodide 511
  oxide 511
  potassium chloride 511
  sodium chloride 511
Platino-chlorides 512
  cyanogen 614
  nitrates 511
Platinoso chlorides 512
Platinous bromate 511
  chloride 511
  hydrate 511
  iodide 511
  oxide 511
  sulphide 511
  sulphite 511
Platinum 509
  history, natural history ; extraction ; properties ; uses . 509-511
  action on water of . . . 228, 420
  bases produced by the action of ammonia on the chlorides of platinum (platinamines) . . 513
  binoxide of 511
  black 10, 510
  compounds of 511
  —reactions of the 514
  oxygen with 511
  chlorine with 512
  sulphur with 514
  power of, for absorbing gases 10, 231, 284
  protochloride of 512
  spongy 510

PAGE
Platinum—*continued.*
  tetrachloride, perchloride or bichloride of 512
Platoso tetrammonic chloride . . 513
  —hydrate 513
  diammonic chloride 513
Plumbago or black lead . . 198, 199
Plumbates, The 525
Plumbic acetate 523, 702
  ammonic sulphate 528
  arsenate 520, 529
  borate 529
  bromide 523
  carbonate 523
  chloride 523, 526
  chlorite 328
  chlorosulphide 528
  chromate 416, 520, 529
  —basic 416
  —as an oxidizing agent . 416, 562
  dithionate 528
  ethide 757
  ferricyanide 613
  ferrocyanide 613
  fluoride 523
  hydrate 524, 525
  iodide 523, 526
  mellonide 612
  molybdate 520
  nitrates 523, 527
  —basic 523
  nitrites 523, 527
  oxide 523, 524
  —use in storage batteries . . . 20
  oxychloride 52, 523, 526
  oxyiodide 527
  peroxide 523, 525
  phosphates . . . 150, 520, 523, 529
  selenate 196
  selenide 194, 523
  silicate 522, 529
  sulphantimonite 594
  sulphate 523, 528
  sulphide 523
  sulphite 523, 528
  sulphochloride 523, 527
  sulphocyanate 612
  tungstate 520, 553
Plumbous oxide 523, 524
  sulphide 523
Pneumonia, absence of chlorine in the urine in cases of 88
Podophyllum resin 653
Poling copper 455
Pollux 367
Polymerism 59, 60
Polyterpenes 634
Populin 687
Porcelain and pottery 444
  mode of manufacture . . 444, 446
Porphyry 443
Portland cement 382
Potash (potassic hydrate) . . 342, 348
  table showing the percentage amount of, in aqueous solu-

PAGE
Potash—*continued.*
    tions of various specific gravities 838
  alum 438
  anhydrous (potassic oxide) 342
  caustic (potassic hydrate) 342
  red prussiate of 346
  yellow prussiate of 345
Potassa sulphurata 346
Potassium 340
  history, natural history, preparation, properties 340
  amalgam 539
  reactions of the compounds of 352
  table of compounds of potassium 341
Potassium acetate 302
  aluminate 439
  aluminic bromide 440
  aluminic silicate 335
  aluminic sulphate (*see* Alums) 441
  amide 342, 351
  antimonate 341, 492
  antimonious tartrate 342, 351, 723
  arsenate 332, 341
  arsenite 334
  aurate 507
  benzoate 672
  bicarbonate 348
  bichromate 414, 415
  bisulphate 347
  bitartrate 351
  borate 336, 342
  borofluoride 221
  bromate 342, 351
  bromide 345
  carbonate 341, 347, 348
  —boiling point of saturated solution of 238
  chlorate 13, 342, 350
  chloride 341, 344
  chlorochromate 417
  chromate 414, 415
  chromic sulphate 417
  cobaltic nitrite 427
  cobaltous sulphate 426
  cupric sulphate 462
  cyanate 607
  cyanide 341, 345, 607, 609
  cyanurate 608
  dioxide 341, 342
  dithionate 320, 341
  ferrate 407
  ferric chloride 408
  —sulphate 410
  ferricyanide 341, 346
  ferrocyanide 341, 345
  ferrous ferricyanide 613
  ferrous ferrocyanide 613
  fluoride 341, 345
  fluosilicate 336, 341, 345
  formate 210, 214
  hydrate 341, 342
  hydric fluoride 341
  —sulphide 346
  —tartrate 351, 342

PAGE
Potassium—*continued.*
  hydride 311, 341
  hydroxide 342
  iodate 325, 342, 351
  iodide 341, 344
  iridic chloride 518
  manganate 395
  manganite 394
  mellonides 612
  mercaptide 679
  metaphosphate 341
  nitrate 140, 320, 342
  —boiling point of saturated solution of 238
  —determination of value of 323
  nickelous cyanide 613
  nitrite 342, 350
  orthophosphate 341
  osmate 476
  osmite 476
  oxalates 720
  oxide 341, 342
  palladic chloride 472
  palladous chloride 472
  perchlorate 327, 342, 351
  periodate 342, 351
  permanganate 589
  peroxide 341, 342
  perruthenate 477
  persulphide 346
  phosphite 351
  platinic-chloride 344, 511
  plumbate 525
  pyrophosphate 341
  pyrosulphate 341, 347
  pyrosulphite 341
  rhodic sulphate 474
  ruthenate 476, 477
  selenate 196, 314, 342
  selenite 319
  silicate 349
  silico-fluoride 341, 345
  sodic tartrate 342, 351
  stannate 481
  stannite 481
  sulphantimonate 341, 494
  sulpharsenate 341
  sulphate 341, 347
  sulphides 341, 346
  sulphite 341, 347
  sulph-hydrate 341, 346
  sulphocyanate 612
  sulphocyanide 608, 612
  tartrate 342, 351, 722, 723
  tellurate 315, 342
  tetrachromate 190, 416
  thiosulphate 341, 347
  titanate 486
  titanofluoride 485
  trichromate 406
  trithionate 196
  vanadate 504
Pottery, Porcelain and 444
Praseodymium 450
Precipitation 5

PAGE
Prefixes 29
Prehnite 443
Prepare liquor 482
Pressure, average, of the air in England 39
  standard 39, 237
Preston smelling salts 371
Proof spirit, meaning of term . . 664
Propane 624
Propene 630
Propine 633
Propione 748
Propionates, The 704
Propionitrile 762
Propylbenzene 637
Propylene 630
Propylic acetate 742
  isosulphocyanide 613
Propyliodide 626
Propylmethylbenzene 634
Proteid, coagulated 797
Proteids 794
  reactions of the 798
"Proto," the prefix 29
Protoxide of nitrogen 128
Prussian blue 617
Prussiate of iron (prussian blue) . 617
  of potash (red) 345, 616
  —(yellow) 345, 614
Prussic acid 605
Pseudocumene 634
Psilomelane 394
Psychrometers 123
Ptyalin 819, 820
Puce or brown lead oxide . . . 525
Pucherite 504
Puddling of iron 401
Pumice stone 443
Purple of Cassius . . 484, 508, 509
Purpureo-cobaltic chloride . . . 427
Purree or Indian yellow 784
Pus 823
Putrefaction, definition of . . . 587
  conditions necessary for . . . 587
  means of preventing 588
Putty powder 479, 481
Pyin 823
Pyrantimonates, The 491
Pyrargyrite 530
Pyrene 592, 646
Pyrethrin 653
Pyridine 592, 754
Pyrites 171
  iron 171
  copper 171
Pyro acid, definition of 29
Pyrocatechin 675, 716, 737
Pyrochroit 393
Pyrogallol 657, 677, 736, 737
Pyrographitic oxide 199
Pyroligneous ether 662
Pyrolusite 88, 391, 394
Pyrophorus (Homberg's) 442
Pyrophosphates, The . . . 165, 329
Pyrophosphorylic chloride . . . 169
PAGE
Pyrophyllite 335
Pyrosulphuric chloride 193
Pyroxylic spirit 662
Pyroxylin 790
Pyrrol 754

Q.

Quadratic system 66
Quantivalence or atomicity of a body 47
  method of determining the . . 49
Quartene 630
Quartine 633
Quartz, crystalline variety of silica, 221, 222, 443
Quercitrin 686, 785
Quicklime 381
Quicksilver (*see* Mercury) . . . 538
Quinicine 772
Quinidine 772, 773
Quinine 772
  tests for 780
Quinine, iodosulphate of . . 769, 773
Quinoidine 772, 773
Quinoline 592
Quinones 624, 645
Quintine 633
Quintone (valylene) 634

R.

Radicals, compound 32, 36, 58, 557, 605
  chemistry of, (Liebig's definition of organic chemistry) . . . 557
Rain water 123, 127
  nitrates in 140
Rangoon tar 647
Realgar 495, 496, 500
Red antimony ore 494
  copper ore 453, 458
  hæmatite 399, 406
  lead ore 416
  manganese ore 391
  ochre 399
  phosphorus 152
  prussiate 346, 616
  silver ore 530
  zinc ore 418
Red bole 444
Red coloring matters 785
Red lead 525
Red liquor of alkali works . 354, 358
Red precipitate 541
Redruthite 461
Refinery iron 401
Refinery slag 410
Regelation, phenomenon of . . . 236
Regular system of crystallisation . 65
Reinsch's test for arsenic 503

PAGE
Reiset's first base 513
  second base 513
"Reiset's first base," chloride of 513
"Reiset's second base," chloride of 513
Relative weight of gases 42
Rennet 586, 796
Resinification 81
Resins 652
  preparation, properties, 652; varieties, uses, 653.
  gum 654
  oleo- 654
Resists in dyeing 788
Resorcin 675
Respiration 81
  amount and character of air needed for 82
  air vitiated by 126
Reverberatory furnace 210
Rhodic chloride 474
  nitrate 474
  oxides 474
  sulphate 474
  sulphite 474
  sulphides 474
Rhodium 473
  history, natural history, extraction, properties 473, 474
  compounds of 474
  —reactions of the 474
Rhodous oxide 474
  sulphide 474
Rhombic system of crystallisation 66
Rhombohedric system of crystallisation 66
Rhubarb 719
Rhubarb resin 653
Rinman's green 424, 427
Rochelle salt 338, 351, 723
Rock crystal 222
Rock oil 647
Rock salt 355
Roman cement 382
"Ropy" condition of wines 580
Rosaniline (aniline red) 758
Rose's metal 464
Rosin, common 653
Rottlerin 653
Rouge, jewellers' 405
Rubian 785
Rubidine 754
Rubidium 366
  borate 336, 367
  bromide 367
  carbonates 367
  chlorate 367
  chloride 367
  dithionate 367
  hydrate 367
  iodide 367
  nitrate 367
  perchlorate 367
  sulphates 367
  spectrum of 367
Ruby 437

PAGE
Russell, analysis of dew 123
  estimation of organic matter in air 127
  estimation of CO_2 in air 125
Rust 403
  ammonia in 259
Ruthenates, The 476
Ruthenic acid 477
  anhydride 477
  chlorides 477
  hydrate 477
  iodide 477
  oxides 477
  peroxide 477
  sulphate 477
  sulphide 477
Ruthenium 476
  history, natural history, extraction, properties 476
  compounds of 477
Ruthenous chloride 477
  oxide 477
Rutile or iron sand 484
Rutylene 633

S.

Saccharates, The 683
Safflower 785
Saffron 785
Sal ammoniac 259
Sal gem 355
Sal alembroth 544
Sal prunelle balls 348
Salicin 686
Salicylol 746
Saligenin 675, 686
  series 674
Saline matters in the air 125, 128
Saliva 819
  composition per 1000 parts of 819
Salt cake process 357
Salt, common (sodic chloride) 355
  bay 355
  cake 356, 357
  Everitt's white 613, 618
  glazing 446
  microcosmic 164, 329, 372
  Schleppe's 333
Salts 291
  acid, definition of 295
  action of salts on 10
  basic 295
  binary theory of 292
  definition of 295
  double; definition of 296, 337
  —haloid 337
  dualistic theory of 292
  effect of heat upon 6
  general history of 291
  haloid 295
  —definition of 295
  in solution, action of acids on 8

PAGE
Salts—*continued.*
  in solution, action of bases on . . . 9
  normal, definition of 295
  oxy- 311
  —definition of 295
  oxysalts 337
  —sulphur 337
  spirits of 250
  sulpho, definition of 269
  varieties of 295
Saltpetre 320, 348
  flour 321
  Chili 320
Saltpetres (nitrates) 320
Samarium 451
Samarskite 451
Sand 123
Sandarach 653
Sandiver 363
Santaline 785
Saponification by lime 735
  by steam 736
  by sulphuric acid 735
Saponin 689
Sapphire 437
Sarcine 776, 803
Sarcocine 703, 776, 802
Saturated solutions 240
  vapors 237
Scagliola, or artificial marbles . . 384
Scales (fish) composition of . . . 800
Scandium 451
Scandous oxide 451
Scheele's acid, preparation of . . 606
  green 334, 462, 499
Scheelite 553
Schleppe's salt 333, 494
Schultz's process for estimating nitrogen 259
Schweinfurt green 334, 463
Sclerogen 789, 791
Scotch soda 106, 357
Scott's cement 382
Sea-water, analyses of . . . 246, 355
  iodine in 106
  silver in 530
Secondary action in electrolysis . 20
  batteries 20
Sedative salt 219
Seignette's salt 723
Selenates, The 314
Selenetted hydrogen 270
Selenides, The 310
Seleniferous sulphur 194
Selenio-cyanates, The 613
Selenite 379, 383
Selenites, The 319
Selenium 194
  history, natural history, preparation, varieties, 194; properties, 195.
  compounds with oxygen . . . 195
  —with chlorine 196
  —with carbon and sulphur . . 196
Seleniuretted hydrogen 270

PAGE
Senarmonite 490
Sepia 786
Septene 630
Ser-albumen 795, 814
Sericin 803
Serpentine 335, 390
Serum 813
"Sesqui," the prefix 29
Sesquichlorides 301
Sesquioxides 297
Sesquiterpenes 634
Sewer gas, sulphuretted hydrogen in 266
Sexdecene 630
Sextene 630
Sextine 633
Shamoying, mode of 737
Sheep dipping mixtures 499
Shellac 653
Shells, composition of 800
Sienna 444
Silica 222
  dialysed 224
Silica in water prevents solution of lead 522
Silicates 335
  definition, natural history, 335; varieties, preparation, properties, 336.
  double 336, 338
Silicic acid 223
  anhydride 222
  chloride 224, 766
  ethide 766
  ethylate 766
  fluoride 225
  hydride 278
  —synonym, preparation, properties 278
  hydrotrichloride 278
  iodoform 279
  methide 766
  methylate 766
  nitride 226
  sulphide 226
  tetrabromide 224
  tetrachloride 224
  tetrafluoride 224, 225
  tetriodide 224
  tribromide 225
  trichloride 225
  trichlor-sulphydrate 225
  triiodide 225
Silicides, The 311
Siliciuretted hydrogen 278
Silico-fluorides (fluo-silicates) . . 336
Silico-formic acid or Leukon 226, 279
Silicon or Silicium 221
  history, natural history, varieties, preparation, 221; properties, 186.
  compounds with oxygen . . . 222
  —with the haloids 224
  —with hydrogen 278
  adamantine (crystalline) . 221, 222

PAGE
Silicon or Silicium—*continued.*
  amorphous 221, 222
  dioxide 222
  graphoidal 221, 222
  hydride of 278
Silicon bromoform 224
  chloroform 224, 278
  formanhydride 226, 279
  iodiform 224, 279
Silk 803
Silver 530
  history, natural history, extraction, properties, uses 530-532
  absorption of oxygen by, when molten 74
  amalgam 530
  compounds of 532
  —with oxygen 533
  —with chlorine 534
  —with sulphur 536
  extraction of, from lead 521
  frosted 531
  fulminating 533
  oxidized 531
  oxy-salts of silver 536
  protoxide of 533
  reactions of the salts of 537
  selenide of 194
  subchloride of 534
  suboxide of 533
  transparency of 281
Silver salts of (*see under* Argentous *and* Argentic).
Silver glance 530, 536
Size 803
Skin 737
Slaked lime 381
Slate 443
  hornblende 443
  mica 443
"Slip" 445
Smalt 427, 429
Smithy scales 403, 406
Smoke nuisances 207
Snow, line of perpetual 119
Soap, hard 354, 734
  soft 735
  marine 354
  arsenical 499
  boilers' waste 441
Soaps 732, 734
Soda 354
Soda, table showing percentage amount of, in aqueous solutions of various specific gravities, 839.
  alum 438
  ash 358
  —impurities of 358
  —purification of 358
  ash process 357
  ball 358
  bicarbonate of 360
  caustic 354
  chloride of 589

PAGE
Soda—*continued.*
  common washing 357
  muriate of 355
  Scotch 357
  waste 358, 383
Sodium 352
  amalgam 539
  history, natural history, preparation, properties 352
  table of compounds of 353
  reaction of the compounds of 365
Sodium acetate 702
  aluminic chloride 440
  aluminate 439
  amide 353
  ammonic hydric phosphate 164, 329
  antimonate 333, 492
  antimonite 334
  argentic thiosulphate 532
  arsenate 331, 332, 353, 500
  biphosphate 362
  bisulphate 357
  bisulphite 357
  boiling point of saturated solution 238
  borate 353, 361
  bromate 353, 361
  bromide 353, 356
  carbonate 353, 357
  —ammonia soda process for preparing 359
  —boiling point of saturated solution 238
  —Leblanc's process for preparing 357
  chlorate 353, 360
  chloride 241, 353, 355
  —boiling point of saturated solution 238
  cyanide 607
  dioxide 353, 354
  dithionate 320, 353
  ethide 767
  ferrate 407
  fluoride 353, 356
  fluosilicate 353
  hydrate 353, 354
  hydride 311, 353
  hydroxide 354
  hyposulphite 95, 188, 318, 353, 357
  iodate 353, 361
  iodide 353, 356
  iridic chloride 518
  manganate 395
  metabismuthite 466
  metantimonite 334
  metaphosphate 329, 330, 353, 357
  nitrate 140, 320, 353, 360
  nitrite 353, 360
  nitro-prusside 613
  oxalate 214, 720
  oxide 353, 354
  perchlorate 353, 361
  periodate 327
  periodide 353, 361

PAGE
Sodium—*continued.*
  phosphate 164, 329, 353, 361
  platinic chloride 511
  polysulphides 353
  potassic carbonate 353, 360
  potassic tartrates 723
  pyrophosphate 329, 330, 353, 362
  pyrosulphite 353
  rhodium sulphate 473
  selenate 353
  sesquicarbonate 353, 360
  silicate 353, 362
  silicofluoride 353
  stannate 317, 483
  sulphantimonate 353, 494
  sulpharsenate 333, 350, 353, 502
  sulpharsenites 334, 501
  sulphate 353, 356
  sulphide 353, 356
  sulphite 353, 357
  sulphophosphate 194
  tartrates 723
  tellurate 353
  thiosulphate 95, 188, 318, 353, 357, 359
  tungstate 317
  zincate 421
Soil, as a natural disinfectant 588
Soils, formation of 213, 791
Solanin 686
Solder 480
Solids, solubility of, in water 240
  homogeneity of 3
  animal 794
Soluble glass 362
Solution 7, 240
  fractional 3
  supersaturated 241
Solutive water (*see* Acid, nitric).
Sombrerite 379
Soot 200
Soranjee 784
Sorbite 686
Sorrel 719
Spar, heavy (barium) 375
Spartein 770, 771
Spathic iron ore 410
Spathose iron ore 399
Specific gravities, tables of 840, 841
  —of bodies, affinity measured by reference to the 21
  gravity of gases 42
Specific heat 45, 283
  heats of elementary bodies 45
  —table of 46
Specular iron ore 339, 406
Speculum metal 456, 480
Speiss 429
Spelter (zinc) 418, 419
Spent oxide 172
Spermaceti 657, 698
Spheroidal condition, The 239
Spiegeleisen 401
Spinelle ruby 438, 439
Spirea, oil of 602, 746

PAGE
Spirit making, alcoholic fermentation in 586
Spirit of salts 250
Spirits of vinegar 701
Spirits of wine (*see* Alcohol).
Spiritus Mindereri 702
  nitro-aërius 68
"Spitting" of metals 74, 510, 531
Spodumene 365
Stalactites and stalagmites 384
Stannates, The 317, 481, 508
Stannic acid 479
  bromide 480
  chloride 480
  ethide 767
  fluoride 480
  iodide 480
  nitrate 479
  oxides 480
  sulphate 479, 481
  sulphide 480
Stannico-fluorides, The 483
Stannites, The 481
Stannous bromide 480
  chloride 480, 482
  ethide 767
  fluoride 480
  hydrate 480, 482
  iodide 480
  nitrate 479
  oxide 480
  oxychloride 480
  stannate 480
  sulphide 480
  sulpho-stannate 483
Starch 687
  common 687
  —preparation, properties, action of heat, action of acids, action of alkalies, action of haloids 687, 688
  iodide of 109
  reactions of 690
Starches 687
  natural history, preparation, varieties 687
Steam, latent heat of 239
Stearates, The 706
Stearin 676
Steatite 335, 390
Steel, preparation of 402, 403
  blistered 402
  natural 402
  occlusion of gases by 402
  shear 402
  tempering 402
Stereochromy 362
Stibethyl 763
Stibine 489, 646
Stibines 763
Stibnite 488
Stilbite 443
Stochiometry 31
Stoneware 446
Storage batteries 20

PAGE

- Strontia . . . 378
- Strontianite . . . 379
- Strontium . . . 378
  - history, natural history, preparation, properties, 378
  - compounds of . . . 378
  - —reactions of the . . . 379
  - spectrum of . . . 379
  - bromide . . . 378
  - carbonate . . . 378, 379
  - chlorate . . . 378
  - chloride . . . 378
  - dioxide . . . 378
  - dithionate . . . 320, 378
  - fluoride . . . 378
  - hydrate . . . 378
  - iodide . . . 378
  - nitrate . . . 378, 379
  - oxide . . . 378
  - peroxide (dioxide) . . . 378
  - phosphate . . . 378
  - silico-fluoride . . . 378
  - sulphate . . . 378
  - sulphite . . . 378
  - thiosulphate . . . 378
- Strychnine . . . 774
  - tests for . . . 11, 781
- Stucco . . . 384
- Styrolene . . . 274, 640
- "Sub," the prefix . . . 30
- Sub-carburetted hydrogen . . . 271
- Suboxides . . . 297
- Substitution, inorganic . . . 57
  - inverse . . . 602
  - organic . . . 58, 93
- Succinamide . . . 761
- Succinimide . . . 695, 760
- Succinylchloride . . . 695
- Sucrates, The . . . 682
- Sucrose . . . 680
- Sucroses, The . . . 680
- Suffioni . . . 219
- Sugar . . . 680
  - action of yeast on . . . 581
  - cane or sparkling . . . 680
  - —natural history, 680; preparation; sugar refining; properties; action of heat, solubility, action of acids, action of alkalies; action of oxidizing bodies, 680-683
  - granular (grape sugar) . . . 684
  - grape . . . 579, 680, 684
  - —history, preparation, properties, action of heat, 684; action of acids, 685.
  - inverted . . . 682, 685
  - milk . . . 680, 683
  - —natural history, preparation, properties, solubility, action of heat, 683
  - mucoid . . . 685
  - muscle . . . 686
- Sugar of lead . . . 703
- Sugars, reactions of the . . . 690

PAGE

- "Sulph" or "Sulpho," the prefix . 30
- Sulphantimonates, The . . . 333, 494
- Sulphantimonites, The . . . 334, 494
- Sulphates, The . . . 311
  - definition, natural history, varieties and constitution, 311; preparation, properties, 312; tests, uses, 314.
  - acid . . . 311, 337
  - allies of the . . . 314
  - basic . . . 312
  - double . . . 312, 337
  - oxy- . . . 313
- Sulph-hydrates, The . . . 309
- Sulphides, The . . . 268, 306
  - definition, natural history, preparation, 306; properties, 307; tests, estimation, 309.
  - classification of the . . . 307
  - double . . . 337
  - oxy- . . . 308
- Sulphites, The . . . 179, 319
  - definition, preparation, properties, tests, uses, 319.
- Sulpho-acids . . . 176, 632
  - bismuthites . . . 464
  - carbamide . . . 708
  - carbonates . . . 217, 308
  - cyanates (sulphocyanides) . . . 612
  - —tests for the . . . 620
  - (or thio-) ethers . . . 741
  - ferrites . . . 409
  - phenyl-urea . . . 755
  - platinates . . . 514
  - stannates . . . 317, 483
  - sulphates . . . 317
  - urea . . . 611, 708, 755
- Sulphur . . . 172
  - synonyms and history, 172; preparation, 172; varieties, 172; properties, 173; uses, 175.
  - allotropic forms of . . . 172
  - estimation of, in an organic body 567
  - form of crystals of . . . 173
  - recovery of, from tank waste . 359
  - specific gravity of vapor of . . 174
- Sulphur, auratum . . . 494
  - black . . . 193
  - bromide . . . 192
  - chloride . . . 191
  - dichloride . . . 191, 192
  - dioxide . . . 176
  - diphosphide . . . 193
  - flowers of . . . 172, 176
  - for gunpowder . . . 349
  - hexiodide . . . 192
  - iodide . . . 192
  - liver of . . . 346
  - milk of . . . 173, 176
  - native . . . 171
  - negative and positive . . . 175
  - oil of . . . 181
  - plastic . . . 173
  - precipitatum . . . 176
  - roll . . . 172

PAGE
Sulphur—*continued.*
  seleniferous 194
  sublimatum 176
  tetrachloride 191, 192
  tetraphosphide 193
  trioxide 180
  urea 611, 755
  virgin 171
  volatile spirits of 176
Sulphurets (*see* Sulphides).
Sulphuretted or hepatic waters . 266
  hydrogen absorption by carbon of 204, 266, 592
  —absorption coefficient of . . 242
Sulphuric acid 176, 180
  —synonyms, history, natural history, and preparation, 180 ; varieties, 183 ; impurities and tests for the impurities of sulphuric acid, 184 ; purification, 184 ; properties, 185 ; uses, 157.
  —action on the metals of . . . 286
  —anhydrous . . . .
  —boiling point of 185
  —glacial 183
  —Graham's 183
  —specific gravity at different peratures 185
  —Nordhausen 181, 183
  —and water, table showing the heat and condensation resulting from mixtures of . 186
  — —on organic matters . . . 186
  —table showing the percentage of real, corresponding to various specific gravities of aqueous sulphuric acid . . 836
Sulphuric ammonide 367
  oxide 180
  oxychlorhydrate 193
  oxydichloride 193
Sulphuric anhydride . . . 176, 180
  —synonyms, preparation, properties 180
Sulphurous acid 176, 179
  anhydride 176
  —synonyms, history, 176 ; natural history, preparation and properties 177
  —tests, uses 179
  absorption coefficient of . . . 242
  —by carbon 204
  oxydichloride 192
Sulphuryl, chloride 178
  chlorhydrate 193
  dichloride 193
Sumbul root 711
Sun, elements detected in atmosphere of the 227
Superheated vapors and liquids 239, 241
Superior affinity 5
"Superphosphate" 151, 164
Supersaturation 241
Surface action 10

PAGE
Sweat 833
Symbols (chemical) and formulæ 30
Sympathetic ink 426
Syngenite 379
Synthesis and analysis 27
Syntonin 797

T.

Tachydrite 389
Tagilite 463
Talc 335, 390
Tallow 734
Tannin 687
Tanning, mode of 737
Tank waste 172, 188, 358
Tannins 736
Tantalates, The 505
Tantalum 504
  compounds of 505
Tar, coal 595
  — — distillation of 266
  wood 596
  Rangoon, or rock oil 647
Tartar, cream of 722
Tartar emetic . . . 351, 342, 490, 723
Tartar of teeth 819
Tartar of wine casks . 340, 351, 722
Tartrates, The double 338
Taurin 822
Tawing, mode of 737
Teeth, composition of the 800
— tartar of 819
Tellurates, The 315
Telluretted hydrogen 270
Telluric bismuth 196
  oxide 196, 197
Tellurides, The 310
Tellurites, The 197
Teichmann's hæmin crystals . . 813
Tellurium 196
  history, natural history, properties 196
  compounds of tellurium and oxygen 197
Tellurous oxide 197
Temperature, standard 40
  average, of the air in England . 119
  influence of, on solubility . . 241
Tenacity of bodies 282
Tension of gases 237
Terbium 451
Terebene 649
Terebenthene 649
Terminations of chemical words . 28
Terpinole 649
Tetra-allyl-ammonic hydrate . . 753
Tetra-butyl-ammonic hydrate . . 753
Tetrachlorides 301
Tetrachlormethane 628
Tetradecane 624
Tetrad elements 50
Tetrahydric pyrophosphate . . . 163
Tetramethyl-ammonic hydrate . . 752

PAGE
- Tetramyl-ammonic hydrate . . . 753
- Tetramylene . . . 630
- Tetrane . . . 624
- Tetramines . . . 750
- Tetraphenylbenzene . . . 646
- Tetraphenylethylene . . . 646
- Tetrathionates, The . . . 320
- Tetrethyl-ammonic hydrate . . . 753
- Thallic bromide . . . 551
  - chloride . . . 551
  - hydrate . . . 551
  - iodide . . . 551
  - nitrate . . . 551, 552
  - oxide . . . 551
  - sulphate . . . 551, 552
  - sulphide . . . 551, 552
- Thallium . . . 550
  - history, natural history, extraction, properties . . . 550
  - compounds of . . . 551
  - —reactions of the . . . 552
- Thallous bromide . . . 551
  - carbonate . . . 551, 552
  - chloride . . . 551, 552
  - fluoride . . . 551
  - hydrate . . . 551
  - iodide . . . 551
  - nitrate . . . 551, 552
  - oxide . . . 551
  - oxyhydrate . . . 552
  - phosphates . . . 551
  - sulphate . . . 551 552
  - sulphide . . . 551, 552
- Thebaine . . . 773
- Theine . . . 774
- Thénard's blue . . . 427, 446
- Theobromine . . . 775
- Thermochemistry . . . 14
- Thermometer, table for converting degrees of the Centigrade into degrees of Fahrenheit's scale . 844
  - wet and dry bulb . . . 123
- Thermometers, hypsometric . . . 237
- Thio-acids . . . 176
- Thio-alcohol . . . 679
- Thio-cyanates . . . 612
- Thio-ethers . . . 741
- Thionamide . . . 192
- Thionyl chloride . . . 178, 192
- Thialdine . . . 755
- Thiophosphoryl chloride . . . 193
- Thiosulphates or sulpho-sulphates 317
- Thorium (thorinum) . . . 449
  - compounds of . . . 449
- Thymol . . . 672
- Time of combination, affinity measured by the . . . 24
- Tin . . . 478
  - history, natural history, preparation, properties, impurities, uses . . . 478, 480
  - amalgam of . . . 480, 539
  - bichloride and tetrachloride of . 482
  - binoxide of . . . 481
  - block . . . 478

PAGE
- Tin—*continued.*
  - butter of . . . 482
  - compounds of (*see* Stannous *and* Stannic) . . . 480
  - crystals . . . 482
  - disulphide of . . . 483
  - foil . . . 479
  - grain . . . 478
  - mine . . . 478
  - nitromuriate of . . . 483
  - ores of . . . 478
  - oxymuriate of . . . 482
  - plate . . . 479
  - protochloride of . . . 482
  - protosulphide of . . . 483
  - pyrites . . . 478, 483
  - reactions of the salts of . . . 484
  - slag . . . 478
  - stone . . . 478
  - salt . . . 482
  - sesquioxide of . . . 480, 481
  - sesquisulphide of . . . 480
- "Tin prepare liquor" of the calico printer . . . 482
- Tin white cobalt . . . 495
- Tincal . . . 219, 361
- Tinder . . . 199
- Tinning, process of . . . 479
- Titanates, The . . . 486
- Titanic acid . . . 485
  - anhydride . . . 485
  - chloride . . . 485, 487
  - cyanonitride . . . 485, 487
  - fluoride . . . 485
  - nitride . . . 485, 487
  - oxide . . . 485
  - sulphide . . . 485, 487
- Titaniferous iron . . . 484
- Titanium . . . 484
  - history, natural history, preparation, properties . . . 484
  - compounds of . . . 485
  - dioxide of . . . 485
  - protoxide of . . . 485
  - reaction of compounds of . . . 487
  - sesquioxide of . . . 485
- Titanous chloride . . . 486
  - oxide . . . 485
- Tobacco, lithium in ash of . . . 365
- Toffy . . . 682
- Tolane . . . 645, 646
- Toluene . . . 592, 595, 634, 639
  - preparation, properties . . . 639
- Toluidine . . . 754, 757
- Toluyene . . . 646
- Tolylamine . . . 754
- Topaz . . . 87, 438, 440
- Torula cerevisæ . . . 579, 581
- Tragacanthin . . . 689
- Trachyte . . . 443
- Transitional elements . . . 54
- Trehalose . . . 680, 684
- Triad elements . . . 50
- Triallylamine . . . 753
- Triamines . . . 750, 755

PAGE

- Triamyl stibine 764
- Triamylamine 753
- Triamylene 630
- Tribenzylamine 753
- Triborethyl 766
- Tributylamine 753
- Tricalcium phosphate 385
- Trichloraldehyde 745
- Trichlorides 301
- Trichlormethane 628, 622
  - preparation, 532-533; properties, uses 533
- Trichromic tetroxide 412, 414
- Triclinic system of crystals . . . 67
- Tricymylamine 753
- Tridecane 624
- Triethene diamine 754
- Triethylamine 752
- Triethyl-arsine 763
  - bismuthine 764
  - phosphine 763
  - stibine 763
- Trihydric phosphate 163
- Triiodomethane 628
- Trimethylamine 752
- Trimethyl phosphine 763
- Trimethyl stibine 763
- Triphane 365
- Triphylline 365
- Triphenylbenzene 646
- Triple phosphate 390
- Triple phosphate calculus . . . 832
- Trithionates, The 190, 320
- Trixylylamine 753
- Tungstates, The 317, 554
  - definition, uses of the 317
  - reactions of the 555
- Tungsten 553
  - natural history, preparation, properties of 553
- Tungstic acid 553
  - anhydride 553, 554
  - dioxydibromide 554
  - dioxydichloride 554
  - hexachloride 554
  - oxytetrachloride 554
  - pentachloride 554
  - sulphide 554
- Tungsto-tungstates, The 555
- Tungstous chloride 554
  - oxide 553, 554
  - sulphide 554
- Turmeric 785
- Turnbull's blue 613, 617
- Turner's yellow 526
- Turpenes, The 60, 634, 648
- Turpentine, English, from the Scotch fir 648
  - French, from the Pinus maritima 648
  - Venice, from the larch 648
  - isomers and polymers of . . . 651
  - oil of, and its allies 648
- "Turps" 648
  - as a disinfectant 589

PAGE

- Turpeth mineral 295, 543
- Turquoise 442
- Tutenag 429
- Twaddell's hydrometer, degrees on 841
- Twilight 119
- Types, doctrine of 41
- Type metal 290, 483

U.

- Ulmin 589, 682, 685
- Ultramarine, native and artificial . 443
- Umber 444
- Undecane 624
- Unit of heat 45
  - thermal 45
  - of volume 43
- Uramil 829
- Uranates, The 433
- Uranic anhydride 432
  - nitrate 432
  - oxide 432
- Uranite 431
- Uranium 431
  - history, natural history, preparation, properties, uses . 431-432
  - atomic weight of 432
  - compounds of 432
  - —reactions of the 434
  - nitrite 434
  - oxychloride 432
  - vitriol 433
  - yellow 433
- Uranous bromide 432
  - chloride 432
  - fluoride 432
  - hydrate 432
  - oxide 432
  - phosphate 150
  - sulphate 432
  - sulphide 432
- Uranyl, radical 433
- Uranylic bromide 432
  - acetate 433
  - ammonium phosphate 433
  - chloride 432
  - nitrate 432, 433
  - pyrosulphate 432
  - sulphate 432, 433
  - sulphide 432
- Urea 60, 216, 607, 610, 755, 777, 782, 826
  - constitution, preparation, properties 826
  - sulphur 611
- Ureas, compound 827
- Uric acid, some products of the oxidation of uric acid 828
- Urinary calculi 831
- Urine 824
  - composition, properties, constituents 824
  - average composition of normal, and average quantity of the

PAGE
Urine—*continued.*
  various constituents excreted in twenty-four hours 824
  spirit of 259
  preparation of phosphorus from 151

V.

Valency 49
Valentinite 488, 490
Valerates, The 704
Valerylene 633
Valylene 634
Vanadates, The 332
Vanadinite 504
Vanadium 503
Vanadous chloride 504
  oxide 504
Vapor, aqueous, table of the tension of 238
Vapor density 568
  determination of vapor density 569
  application of the facts deduced from ultimate analysis, and from the determination of the vapor densities of organic bodies 572
Vapor tension 237
Vapors, latent heat of 239
Varec 106, 357
Varentrapps' and Wills' process for estimating nitrogen in an organic body 566
Varnishes 654
Varvicite 394
Veget-albumen 795
Vegetable chemistry 789
Vegetable parchment 790
Venetian red 405
Ventilation, air needful for 82, 212
Veratrine 775
Verdigris 463, 703
Vermilion 547
Vinegar, manufacture of 586
  French wine 587
  English malt 587
  springs of volcanic districts 181
Vinic alcohol 663
Vinous fermentation 579
Viridine 754
Viscous fermentation 580
Vital force 557
Vitality, influence of, on chemical action 20
Vitellin 795
Vitriol 181
  cobalt 426
  green 409
  white 422
  iron 409
  lead 528
  oil of 181, 183
  —fuming 183
  spirit or essence of 181

PAGE
Volatile alkali 259
Volatility changed by chemical action 4
Volborthite 504
Volcanic glass 443
Volcanoes, gases in neighbourhood of 227
Volume, meaning of term 37
Volume symbols 37
  of bodies 40
Vulcanite 655

W.

Wad 394
Wash leather 737
Washing soda 357
Water 233
  —history, natural history, preparation, composition, 233; properties, 179-206.
  action on the metals of 228
  as a solvent 240
  boiling point of 237
  —of saturated solutions of various salts in 238
  Clark's process for softening 385
  common (rain, spring and well, lake and marsh, and river) 245
  freezing point of 235
  hardness of 247, 383
  Harrogate 171
  heat developed in the formation of 16, 19
  latent heat of 236
  maximum density of 235, 239
  potable 247
  superheated 241
  tension of the vapor of 238
  unit of heat 45, 236
  —of weight (specific gravity) 235
  weight of 235, 842
  —on various areas 846
Water gas 210
Wavelite 87, 150, 442
Weights of gases, determination of 43
Weights and measures, table of English 841
Weld, or luteoline 784
Welding of the metals 283
Weldon's process for regenerating manganese dioxide 89, 394
Whey 683
White arsenic 498
  lead ore 520, 527
  precipitate 544
  vitriol 422
White lead, preparation of 528
White precipitate 545
White wax 733
Willemite 335
Williamite 418
Winds 119
Wine casks, tartar of 340

PAGE

- Wine-making, alcoholic fermentation in 585
- Wine, ropy state of 580
  - varieties of 585
- Wine, spirits of 657, 663
- Wintergreen, oil of 662
- Witherite (barium carbonate) 377
- Wolfram 478, 553
- Wolfranium 553
- Wood charcoal 199, 200, 598
  - naphtha 597
  - tar 598
- Wood, decay of 589
  - its conversion into coal 205
  - products of the distillation of 596
- Wood or pyroxylic spirit 597, 657, 662
- Woody matter 791
- Wort 585
- Wrought iron 403
- Wurtzite 422

X.

- Xanthin 776, 785, 803, 831
- Xanthoproteic reaction of proteids 798
- Xylene 592, 595, 634, 637
- Xylenol 669
- Xylidine 754
- Xylylamine 753

Y.

- Yeast, a complicated ferment 581
- Yeast, dried 581
- Yellow chrome 315, 416
- Yellow ore 592
- Yellow prussiate 345, 615
- Yellow, ultramarine 415
- "Yl" and "Yle," the terminations 29
- Ytterbium 451
- Yttria 451
- Yttrium 450
  - Crookes's researches on 451
- Yttrous chloride 451
  - nitrate 451
  - oxide 451
  - sulphate 451

Z.

- Zaffre 424, 427
- Zircon 335, 449
- Zirconia 449
- Zirconium 449
  - bromide 449
  - chloride 449

PAGE

- Zirconium—*continued.*
  - fluoride 449
  - hydrate 449
  - oxide 446
  - silicate 335
- Zirconates, The 449
- Zirconofluorides, The 449
- Zinc 418
  - history, natural history, preparation, properties, uses 418, 419
  - blende 418, 421, 422, 443
  - compounds of 421
  - glass 418
  - impurities of 419
  - ores 418
  - reactions of the salts of 423
  - spar 423
  - spinelle 418
  - vapor density of 44
  - white 421
- Zinc acetate 702
  - aluminate 439
  - ammonic chloride 422
  - amylide 767
  - antimonide 421, 422
  - arsenide 421, 422, 497
  - bromide 421, 422
  - carbonate 421, 423
  - chloride 421, 422, 589
  - —a dehydrating agent 602
  - chromite 413
  - cyanide 607
  - ethide 767
  - ethyl 757
  - ferrocyanide 424
  - fluoride 421, 422
  - fluosilicate 422
  - hydrate 421
  - iodide 421, 422
  - methide 767
  - molybdate 516
  - nitrate 421, 423
  - nitride 422
  - oxide 421
  - oxycarbonate 423
  - oxychloride 422
  - pentasulphide 421, 422
  - phosphate 423
  - phosphide 422
  - potassic sulphate 423
  - silicate 335
  - silico-fluoride 421, 422
  - sulphate 421, 422, 589
  - sulphide 421, 422
- Zone of carburation (iron) 400
  - —fusion 400
  - —reduction 400
- Zoolites 443
- Zymotic or ferment diseases 582

WERTHEIMER, LEA AND CO., CIRCUS PLACE, LONDON WALL.

BY THE SAME AUTHOR.

LEGAL MEDICINE,

VOL. I., INCLUDING EVIDENCE.

Contents: The Signs of Death—The Post-Mortem—Sex—Monstrosities—Hermaphrodism—Expectation of Life—Presumption of Death and Survivorship—Heat and Cold—Burns—Lightning—Explosions—Starvation. With Illustrations. Royal 8vo. 25*s*.

VOL. II.

Contents: Legitimacy and Paternity—Abortion—Rape—Indecent Exposure—Sodomy—Bestiality—Live Birth—Infanticide—Asphyxia—Drowning—Hanging—Strangulation—Suffocation. Royal 8vo. 21*s*.

"The most complete Manual of Forensic Medicine in the English language."

VOL. III. IN PREPARATION.

LONDON:
SMITH, ELDER & CO., 15, WATERLOO PLACE.

ALSO,

THE LONDON WATER SUPPLY.

A SERIES OF REPORTS ON THE COMPOSITION OF THE WATER SUPPLIED TO THE METROPOLIS.

LONDON:
J. AND A. CHURCHILL, NEW BURLINGTON STREET.

A few copies of Dr. Meymott Tidy's Papers on

"THE METHODS OF ESTIMATING THE ORGANIC MATTER IN POTABLE WATERS," AND ON "RIVER WATER,"

May be obtained on application to the Printers, Messrs. Wertheimer & Lea, 1½, Circus Place, Finsbury Circus, E.C. Price, 5s.

92